Taylor & Francis
Taylor & Francis Group

REACTIONS OF IMIDAZOL(IN)-2-YLIDENES WITH ELECTRON DEFICIENT FLUOROOLEFINS.

Anthony J. Arduengo, III,[1] Joseph C. Calabrese,[2] H. V. Rasika Dias,[2] Fredric Davidson,[2] Jens R. Goerlich,[2] Alexander Jockisch,[1] Michael Kline,[2] William J. Marshall,[2] Jason W. Runyon[1]

[1]Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487-0336, USA
[2]DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328, USA.

GRAPHICAL ABSTRACT

$R_F = F, -CF_2CF_2-, -CF_2(CF_2)CF_2-$
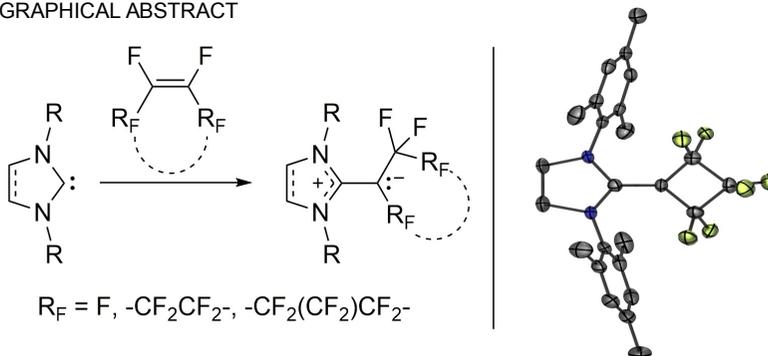
In Memory of Reinhard Schmutzler.

Abstract 1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene forms stable 1:1 adducts with tetrafluoroethylene (**2**), hexafluorocyclobutene (**3**) and octafluorocyclopentene (**4**). Adduct **2** shows properties typical for non-polarized olefins, as indicated by NMR spectroscopy and X-ray crystallography. By contrast, adducts **3** and **4** are best described as ylides with a significant charge separation between the imidazoline ring and the perfluorocycloalkyl unit. Similarly, 1,3-di-1-adamantylimidazol-2-ylidene reacts with tetrakis(trifluoromethyl)-allene to form a polarized trimethylenemethane derivative, and bis(trifluoromethyl)ketene to form an imidazolium enolate zwitterion. The synthesis and characterization of a number of fluorinated methyleneimidazolines are described herein.
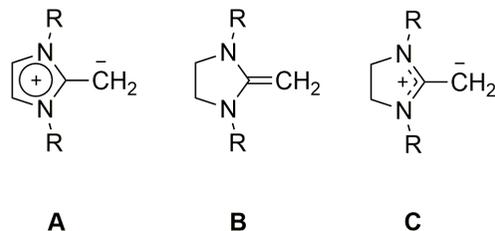
Introduction

2-Methylene-imidazolines and -imidazolidines, formally adducts of the corresponding heterocyclic carbene and a methylene unit ($:CR_2$), are strong bases which possess nucleophilic and electron donating properties due to the high electron density at the exocyclic CH_2-moiety.[1-7] In the case of 2-methyleneimidazolines, charge separation leading to a "ylide" structure (**A**) (Scheme 1) is energetically favored because of the delocalization in the 5-membered ring system.[1] By contrast, due to the lower electron π-density in the ring system and the lack of delocalization, 2-methylenimidazolidines may show a less polar "ylene" structure (**B**) as suggested by NMR spectroscopy and X-ray crystallography.[6-8] In cases where a saturated ring system is present, substitution of the CR_2 fragment by a strongly electron deficient moiety CX_2 (*e.g.* CF_3 or CN) may still favor a ylide-like dipolar structure **C**.[9,10] We recently reported chemistry of imidazol-2-ylidenes with cyano-olefins and we now focus attention on reactions with electron-deficient fluoro-olefins.[11]

Scheme 1. 2-Methyleneimidazol(in)es are represented as resonance structures **A-C**.

RESULTS AND DISCUSSION
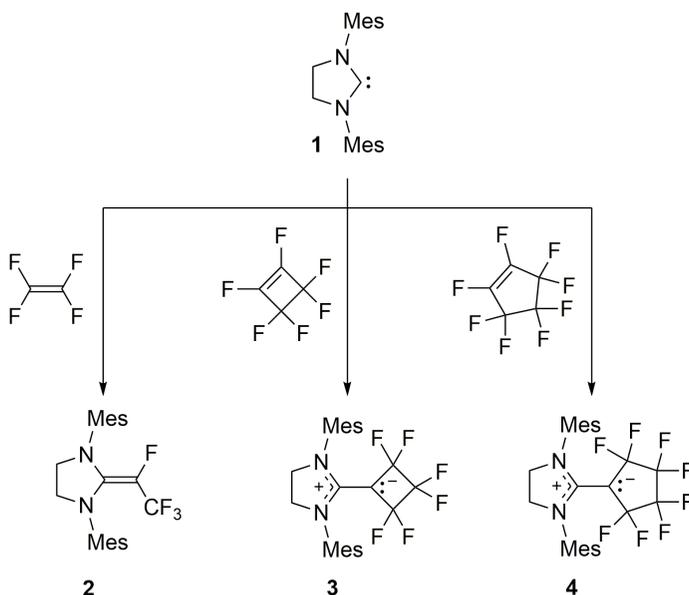
Scheme 2. Addition of fluoro-olefins to **1** yields adducts **2-4**.

Cyclic and acyclic fluoro-olefins readily react with 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene **1** yielding the 1:1 addition products **2**, **3**, and **4** (Scheme 2). The reactions proceed at room temperature, affording **2 - 4** in high yields as air and moisture sensitive compounds that are readily soluble in non-polar organic solvents like toluene, THF, and dichloromethane. The solubility in hexane decreases from **2** to **4** indicating an increasing polar character of the compounds and lowered lipophilicity (or perhaps enhanced fluorophilicity). While it is well known that perfluoro-olefins undergo addition with a wide range of nucleophiles,[9, 12-15] the ease with which the reaction proceeds in the case of tetrafluoroethylene is somewhat surprising.

The likely mechanistic pathway proceeds through nucleophilic addition of the carbene to the fluoro-olefin, first forming zwitterionic intermediates (**D**). Ionization to the fluoride salts, **E**, followed by fluoride re-addition to the other site of the fluoroolefin gives the observed adducts (**F**, Scheme 3). A mechanism involving a [2 + 1] cycloaddition as proposed for the reaction of 1,3,4-triphenyltriazol-5-ylidene with electron deficient olefins can be excluded.[16] The reactivity of the carbene **1** toward perfluoro-olefins resembles that of neutral Group 15 nucleophiles ER_3 (E = N,[17] P,[18-22]As;[23] R = Aryl, Alkyl) which also form 1:1 adducts of ylidic structure. One may consider this as a further analogy of the reactivity of nucleophilic carbenes and tertiary phosphines.[24]

Scheme 3. Proposed mechanism for the formation of ylides.

The ^{1}H NMR spectra of the adducts show only minor differences among the products **2** - **4**. Compared to the free carbene **1** (δ 3.26),[25,26] the resonances for the imidazolidine hydrogen atoms H[4/5] of **2** - **4** are shifted slightly to higher field (**2**: δ 3.06, **3**: δ 2.98, **4**: δ 2.94). The ^{13}C and ^{19}F NMR spectra, on the other hand, reveal significant spectral differences between structures **2** - **4**. The ^{13}C NMR spectra are especially diagnostic as an increase in charge separation from **2** to **4** should be reflected in the δ(C) values for the joined carbon atoms. By contrast, the resonances of the other carbon atoms are expected to be mostly unchanged compared to the free carbene.[26] The ^{13}C NMR spectrum of **2** shows the resonance for the former carbene center C^2 at δ 144.49 (significantly upfield of the free carbene shift of δ 243.77).[26] The chemical shift for the attached fluoromethylene carbon atom is observed at δ 119.29. The substitution of the $\underline{C}(F)CF_3$-moiety in **2** for a perfluorocyclobutyl group in **3,** or a perfluorocyclopentyl group in **4** results in a significant downfield shift of the signal for C^2 (**3**: δ 157.09, **4**: δ 160.41) relative to that observed in **2**, and a strong upfield shift for the attached C atom (**3**: δ 69.73, **4**: δ 66.07). While the δ(C) values found for both of the joined carbon atoms in **2** are in a range typical of olefins,[27] this is no longer true for compounds **3** and **4**. The ^{13}C NMR shifts observed for C^2 are close to resonances reported for C^2 in 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride,[26] and the strong shielding of the "anionic" carbon atom bonded to C^2 is analogous to the findings for δ(C) of the exocyclic CH_2 group in 2-methylenimidazolines and –imidazolidines.[1,8] The simultaneous shielding and de-shielding observed in the ^{13}C NMR spectra of **3** and **4** for the two joined carbon centers clearly indicates the large extent of charge separation in the two compounds. The ^{19}F NMR spectrum of adduct **2** displays resonances and multiplicities as expected for a typical fluoro-olefin.[28] Nevertheless, the signal for the vinylic fluorine atom (δ -205.0) is one of the most negative values observed for vinylic fluorine.[28] This shielding effect is attributed to the strong electron donating properties of the imidazolidine ring system. As expected, the ^{19}F NMR spectra of **3** and **4** each show two resonances for the CF_2 groups at δ –94.9/–128.3 and δ –92.4/–134.5, respectively. While the

Figure 1. X-ray crystal structures of **2**, **3**, and **4**. Thermal ellipsoids drawn at the 50% prob. level.

multiplets in compound **3** are only somewhat distorted, the multiplets in the ^{19}F NMR spectrum of **4** exhibit noticeable high order coupling. This non-equivalence of the CF$_2$ groups in **4** can be explained by the greater flexibility of the perfluorocyclopentyl group as compared to the perfluorocyclobutyl group in **3**. This exchange is fast in solution on the NMR timescale (µs), where at room temperature only average values for the resonances are observed for **3** and **4**. Experiments performed at -80 °C reveal a strong broadening of the signals, but the coalescence point was still not reached. The ^{19}F NMR resonances in **3** (δ -94.9, -128.3) are found Δδ 3.7 - 12.5 ppm upfield of the CF$_2$ groups observed for ylides derived from hexafluorocyclobutene and tertiary amines, phosphines, and arsines.[18,23]

Table 1. Selected Bond Lengths (pm) and Angles (°) for **2 – 4**, **9**, **13**, and **14**.[a]

property	2	3	4	9	13	14
r(C²-N¹(³))	137.5(6), 137.4(6)	133.8(4), 136.7(4) / 134.7(4), 135.1(4)	135.1(3), 136.7(3)	133.5(7), 134.8(7)	136.1(4), 135.3(4)	135.8(6), 135.5(6)
r(N¹(³)-C⁴(⁵))	145.3(6), 146.6(7)	147.3(4), 147.5(4) / 145.3(5), 146.8(4)	146.7(3), 147.0(3)	139.4(7), 1379(7)	137.6(5), 138.4(5)	137.7(6), 137.3(6)
r(C⁴-C⁵)	147.7(8)	149.3(5), 151.0(5)	147.9(4)	149.8(8)	132.2(5)	133.6(7)
r(C²-Cexo)	133.6(7)	140.8(4), 138.2(4)	139.2(3)	146.7(8)	150.5(5)	150.5(7)
θ(N¹-C²-N³)	109.1(5)	109.4(3), 108.6(3)	108.9(2)	107.8(5)	107.8(3)	107.6(5)
θ(N¹(³)-C²-Cexo)	124.8(5), 126.1(5)	126.0(3), 124.6(3) / 125.6(3), 125.8(3)	124.2(2), 126.8(2)	126.0(5), 126.2(5)	126.1(3), 126.1(3)	125.6(5), 126.2(5)
θ(C⁵(⁴)-N¹(³)-C²)	109.8(5), 110.7(5)	110.2(3), 111.6(3) / 111.8(3), 112.4(2)	110.4(2), 111.0(2)	108.2(5), 109.5(5)	107.3(3), 108.2(3)	107.8(5), 108.4(5)
θ(N¹(³)-C⁵(⁴)-C⁴(⁵))	104.9(5), 105.3(5)	103.3(3), 104.1(3) / 102.5(3), 104.2(3)	103.9(2), 104.1(2)	106.0(5), 108.6(5)	109.3(4), 107.5(3)	107.5(5), 108.6(5)
θ(C²-N¹(³)-C⁸)	124.0(5), 125.1(5)	127.0(2), 127.5(2) / 128.0(3), 128.4(3)	126.3(2), 128.4(2)	125.4(5), 126.0(5)	134.1(3), 134.4(3)	129.1(5), 128.7(5)
α(Imid-[C^exo C(F)C])	12.9	6.8, 3.9	19.6	66.8	76.6	90.8

[a] The numbering scheme for all compounds follows IUPAC recommendations.

Crystals of **2 - 4** suitable for single crystal X-ray diffraction studies were grown from saturated hexane or hexane/toluene solutions. All three compounds crystallize in the monoclinic space group $P2_1$/n, but the structures are not isomorphic.[29-32] The geometries of the molecules in the solid state are depicted in Figure 1 and selected bond lengths and angles are summarized in Table 1.

The structural parameters of the 1,3-dimesitylimidazoline moieties of **2 - 4** are similar and in accordance with that of other imidazoline compounds described in the literature.[8,33,34] All three crystal structures show planar imidazoline rings with average N-C² distances of 135.9 pm and average N-C²-N angles of 109.0°. The mesityl rings of **2** and **4** are twisted disrotatory by 76/79° and 74/78° out of the central imidazoline plane, and by 86/89° [87/90°] in **3**. The greater rotation of the mesityl units in **3** is caused by the special posture of the hexafluorocyclobutyl substituent in imidazoline C² position. The nearly planar C$_4$F$_6$ unit (7 pm maximum deviation of a C atom from the best plane) of **3** stands nearly parallel to the imidazoline ring with an inter-plane angle of only 7° and 4° for the two crystallographically independent molecules. By contrast, the C(F)(CF$_3$) plane in **2** and that of the C(CF$_2$)$_2$ moiety in **4** are twisted by 13° and 20° with respect to the pendent imidazolines. The less spatially encumbering (pinned back) C$_4$F$_6$ ring unit of **3** likely allows for a more planar arrangement about the central C-C bond. The perfluoroalkyl substituents of **2 - 4** show characteristic features for fluorinated aliphatics. The cyclo-butylidene group of **3** is almost planar (7 pm maximum deviation of a C atom), while the cyclopentylidene ring of **4** adopts an envelope conformation. The C-C single bonds between the fluoromethylene units and the olefinic (or formally carbanionic center) are somewhat shortened (reflecting some degree of negative hyperconjugation[35]) and comprise the narrow range of 145.3(7) - 147.6(5) pm. The central carbon atoms of the new

C-C bond adopt a trigonal planar geometry in all three compounds. The C-F bond distances are as expected, showing values between 133.9(4) and 138.6(4) pm.

The C²-C bond lengths of structures **2 – 4** reflect the observations from the NMR spectroscopy that suggest increased charge separation between these two "olefinic" carbons. In solution, the ^{13}C NMR shifts also suggest that **2** should exhibit the shortest C²-C distance (and hence lowest degree of charge separation) among the adducts. In the solid state, the structure of **2** reveals a central C-C bond distance of 133.6(7) pm that is characteristic for the non-polarized olefinic double bond, but the corresponding C²-C distances in **3** and **4** are significantly elongated to 140.8(4) [138.2(4)] and 139.2(3) pm, respectively, which makes a more dipolar description of these bonds reasonable. The deviation from linearity of the dihedral angle along the C²-C axis of the perfluoroalkyl groups of **3** and **4** suggest that there is limited π-interactions in the central C-C bond. Interestingly, the extent of pyramidalization of the nitrogen centers also tracks the C-C bond distances in structures **2-4** with the highest degree of pyramidalization observed for **2**.

5 R = Mes, X = H   **7** R = Mes, X = H   **9**
6 R, X = Me   **8** R, X = Me
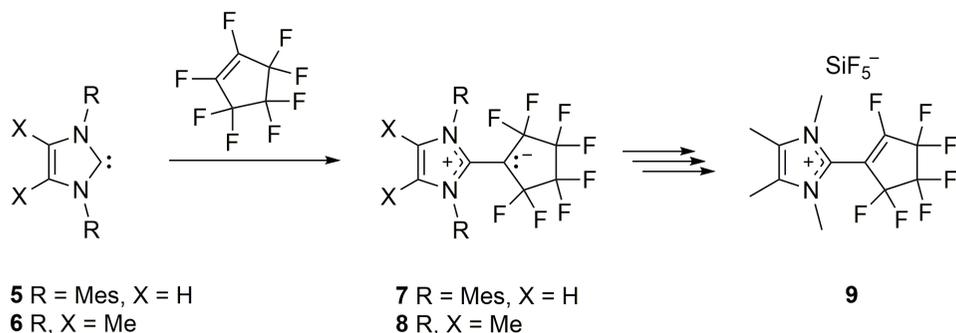
Scheme 4. Addition of fluoro-olefins to unsaturated imidazol-2-ylidenes (**5**, **6**) yields adducts **7** and **8**. Further decomposition of **8** is observed to **9**.

Adducts of the unsaturated imidazol-2-ylidenes with perfluoroolefins were also synthesized. Octafluorocyclopentene reacted smoothly with 1,3-dimesityl-imidazol-2-ylidene to give the polarized olefin **7**. The carbanionic center in **7** resonates at δ 57.56 in the ^{13}C NMR spectrum, substantially upfield of the corresponding centers in **3 & 4** (69.73 & 66.07, respectively). The former carbene center in **7** shows a ^{13}C resonance at δ 148.30 that is also 10-12 ppm upfield of the resonances observed for the same centers in **3 & 4**. These data would be consistent with an even larger degree of charge separation in **7** relative to **3** and **4**, and may be a reflection of the superior

9
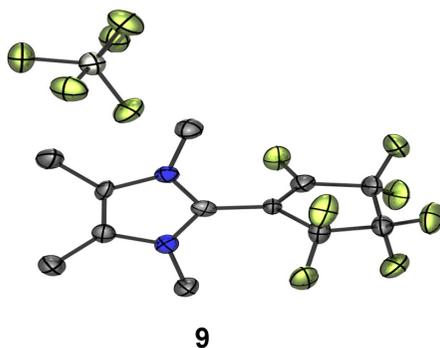
Figure 2. X-ray crystal structure of **9**. Thermal ellipsoids drawn at the 50% probability level.

stability of the delocalized cationic (imidazolium) moiety in **7**. It is interesting that the ease of handling of **7** was not as great as with **2**, **3**, and **4**. It is possible that the weaker nucleophilicity of an imidazol-2-ylidene as compared to an imidazolin-2-ylidene may allow for easier elimination of the nucleophile, or the higher degree of charge separation in **7** may predispose the compound to β-

elimination of a fluoride anion. This latter possibility may be further supported by the observation that the adduct between octafluorocyclopentene and 1,3,4,5-tetramethylimidazol-2-ylidene was difficult to isolate and characterize. From attempts to purify and characterize the reaction mixture containing **8** only a small amount of material was eventually isolated that proved to be the pentafluorsilicate salt **9** (Scheme 4) which was characterized by single crystal X-ray diffraction.[36] Fluoride loss from the imidazol-2-ylidene adducts **7** and **8** may lead to the formation of HF *in situ*, and further reaction with glass ultimately the SiF_5^- anion - supporting the above observation. The serendipitous characterization of the structure of the fluoroolefin-substituted imidazolium ion **9** does, however, provide another reference point for comparative analysis of the polarized olefin structures **2-4**. The central C-C bond in **9**, which represents a single bond between two sp^2 centers in these coupled systems, averages 147.5 pm for the two crystallographically unique molecules. This value is substantially longer (+6.7 – 13.9 pm) than those distances observed for **2-4** in which one expects to see bond shortening due to π-π conjugation and electrostatic interactions.

Nucleophilic additions of 1,3-di-1-adamantylimidazol-2-ylidene to tetrakis(trifluoromethylene)allene or bis(trifluoromethyl)ketene provide further examples of zwitterionic structures derived from additions of N-heterocyclic carbenes to electrophilic π-systems (Scheme 5). For both the polarized tri(methylene)methane adduct **13** and the enolate adduct **14**, highly twisted (nearly

10	**11** E = C(CF$_3$)$_2$	**13** E = C(CF$_3$)$_2$
	12 E = O	**14** E = O

Scheme 5. Addition of allene **11** and ketene **12** to **10** yields adducts **13-14**.

perpendicular) geometries are observed about the central C-C bond suggesting that there is little π-π conjugation.[37,38] Indeed, the central C-C bond distances in these two adducts are 150.5 pm which is even longer than observed for **9**. Increased delocalization in the anionic moiety (enolate in

Figure 3. X-ray crystal structures of **13** and **14**. Thermal ellipsoids drawn at the 50% prob. level.

the case of **14**, and allyl anion in the case of **13**) reduces the need of stabilizing the anionic center through electrostatic and π-π interactions with the imidazolium ion.

Conclusions

1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene forms stable 1:1 adducts with tetrafluoro-ethylene (**2**), hexafluorocyclobutene (**3**) and octafluorocyclopentene (**4**). While the ^{13}C NMR resonances for the two central carbon atoms connecting the imidazoline ring and the perfluoroalkyl unit of **2** (δ 144.49 and 119.29) are within the range of a typical olefin, the same is not true for **3** and **4**. The strong downfield shifts of the signals for the imidazoline C^2 to δ 157.09 (**3**) and 160.41 (**4**) that come along with a strong upfield shift of the resonances of the attached C atoms to δ 69.73 (**3**) and 66.07 (**4**) indicate a significant charge separation along these C^2-C bonds and make a description of **3** and **4** as ylidic compounds reasonable. These findings in solution are corroborated by the solid state single crystal structures of **2 – 4**.[29-32] The C^2-C bond length of **2** is with 133.6(7) pm characteristic for a C=C double bond, but the corresponding bond distances of **3** and **4** are elongated to 140.8(4) and 139.2(3) pm, respectively. The relative posture of the perfluoroalkyl moiety with respect to the imidazoline ring plane is found to be quite flexible in **2**, **3** and **4**, and reflects, at best, only slight π-π conjugation and electrostatic interactions when compared to the salt **9** in which these interactions can be presumed to be totally absent. Although all three compounds bear strong electron withdrawing perfluoroalkyl groups, the experimental data suggest that the imidazoline carbene-tetrafluoroethylene-adduct **2** exhibits the largest degree of "olefinic" character. By contrast, the hexafluorocyclobutene adduct **3** possesses the most nearly planar geometry, but other geometric and spectroscopic parameters suggest that this planar geometry can be explained by the diminished steric demands of the cyclobutyl moiety.

Imidazol-2-ylidene addition adducts to fluoroolefins can also be formed. NMR spectroscopic data for these products suggest a higher degree of polarization of the resulting olefin when compared to adducts from saturated diaminocarbenes. Finally, adducts of imidazol-2-ylidenes with electron deficient fluoroolefins in which delocalization of the anion charge can occur (*e.g.* the adducts derived from tetrakis(trifluoromethylene)allene or bis(trifluoromethyl)ketene) show extremely charge separated zwitterions that can be best categorized as imidazolium enolates (**14**) or polarized trimethylenemethanes (**13**). These last two classes of polarized adducts are reminiscent of the recently reported adducts of imidazol-2-ylidenes with tetracyanoethylene.[11]

Experimental

General Considerations. All moisture and air sensitive reactions and manipulations were carried out in oven-dried glassware under dry nitrogen atmosphere, either in a Vacuum Atmosphere® dry-box or by using standard Schlenk techniques. Unless otherwise noted, reagents were used as obtained from commercial sources. Tetrahydrofuran was dried over calcium hydride then distilled from sodium/benzophenone and stored in the drybox. Hexane, toluene, and Et_2O were distilled from calcium hydride and stored in the drybox. Solvents removed *in vacuo* were done so using a mechanical vacuum pump. Melting points were obtained using a Laboratory Device MEL-TEMP® II apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a GE® Omega-300 MHz spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) using residual solvent protons as the internal standard are reported as referenced to tetramethylsilane (δ scale) with positive shifts downfield using an internal standard (residual protons) from the solvent, C_6D_6 (7.26 ppm) and THF-d_8 (1.73 ppm, 3.58 ppm). ^{13}C NMR spectra are reported in ppm relative to tetramethylsilane (δ scale) using an internal standard from the solvent, C_6D_6 (128.0 ppm) and THF-d_8 (25.5 ppm, 67.7 ppm). [13]F NMR spectra are reported in ppm relative to $CFCl_3$ (δ scale). [14]N NMR spectra are reported in ppm relative to nitrate anion of ammonium nitrate (δ scale). Spectral data are listed as follows: chemical shift (multiplicity, relative number of hydrogen atoms, coupling constant). Multiplicities are denoted as follows: s (singlet), d (doublet), dd (doublet of doublets), dq (doublet of quartets), t (triplet), q (quartet), m (multiplet), br (broad), quint (quintet), sext (sextet), sept (septet). Elemental analyses were performed by Oneida Research Services, Whitesboro, New York, and are reported as relative percent of each element analyzed.

Synthesis of 2. Tetrafluoroethylene was bubbled through a solution of 0.10 g (0.33 mmol) of **1** in 20 mL of benzene for 3 h at room temperature over which time a light yellow color developed. The mixture was stirred for 3 d at room temperature. Evaporation of the solvent gave **2** as a light yellow, oily solid. Yellow needles were obtained by recrystallization from hexane at -25 °C. Yield: 0.117 g (87%); mp. 186 °C. ^{1}H NMR (C$_6$D$_6$) δ = 2.09, 2.10 (s, 6 H, p-CH$_3$), 2.26, 2.27 (s, 12 H, o-CH$_3$), 3.06 (s, 4 H, Im H$^{4/5}$), 6.73, 6.76 (s, 4 H, Ph H$^{3/5}$); ^{13}C NMR (C$_6$D$_6$) δ = 18.04, 18.19 (s, o-CH$_3$), 20.88, 20.92 (s, p-CH$_3$), 49.92, 51.62 (s, Im C$^{4/5}$), 119.29 (dq, J = 197.2 Hz, J = 43.9 Hz, CF), 124.20 (qd, J = 264.3 Hz, J = 33.6 Hz, CF_3), 129.58, 129.89 (s, Ph C$^{2/6}$), 135.67 (q, J = 1.2 Hz, Ph C$^{2/6}$), 135.90 (d, J = 3.0 Hz, Ph C$^{2/6}$), 136.59, 136.79 (s, Ph C^4), 138.25 (d, J = 3.1 Hz, Ph C^1), 139.20 (q, J = 1.2 Hz, Ph C^1), 144.59 (dq, J = 17.1 Hz, J = 1.8 Hz, Im C^2); ^{19}F NMR (C$_6$D$_6$) δ = -205.0 (q, J = 15.5 Hz, 1 F, CF), -60.4 (d, J = 15.5 Hz, 3 F, CF_3); MS (EI, 70 eV); m/z (%): 406 (30) (M$^+$), 405 (40) (M$^+$ - H), 391 (55) (M$^+$ - CH$_3$), 305 (100) (M$^+$ - C$_2$HF$_4$), 246 (15) (M$^+$ - C$_9$H$_{11}$). Anal. Calcd for C$_{23}$H$_{26}$F$_4$N$_2$: C, 67.96; H, 6.45; N, 6.89. Found: C, 67.89; H, 6.63; N, 6.89.

Synthesis of 3. Hexafluorocyclobutene (0.411 g, 2.5 mmol) was condensed at -196 °C *via* a vacuum line to a solution of 0.115 g (0.38 mmol) of **1** in 30 mL of hexane. The reaction was warmed to room temperature after which point the mixture became cloudy and **3** precipitated as a colorless solid. After stirring for 20 h at room temperature, the precipitate was filtered off and dried *in vacuo*. Yield: 0.144 g (81%); mp. 242 °C (dec); ^{1}H NMR (C$_6$D$_6$) δ = 2.07 (s, 6 H, p-CH$_3$), 2.20 (s, 12 H, o-CH$_3$), 2.98 (s, 4 H, Im H$^{4/5}$), 6.77 (s, 4 H, Ph H$^{3/5}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = 17.59 (s, o-CH$_3$), 21.02 (s, p-CH$_3$), 49.42 (s, Im C$^{4/5}$), 69.4-70.0 (m, C^2-C), 111.7-120.5 (m, CF$_2$CF$_2$CF$_2$, CF$_2$CF$_2$CF$_2$), 129.80 (s, Ph C$^{3/5}$), 133.25 (s, Ph-C^1), 137.16 (s, Ph C$^{2/6}$), 139.02 (s, Ph C^4), 156.9-157.3 (m, Im C^2); ^{13}C{^{19}F} NMR (C$_6$D$_6$) δ = 17.59 (q, J = 130.03 Hz, o-CH$_3$), 20.97 (q, J = 130.60 Hz, p-CH$_3$), 49.39 (t, J = 145.26 Hz, Im C$^{4/5}$), 69.73 (s, (C^2-C), 115.97 (s, CF$_2$CF$_2$CF$_2$), 116.42 (s, CF$_2$CF$_2$CF$_2$), 129.94 (d, J = 140.19 Hz, Ph C$^{3/5}$), 132.8-133.8 (m, Ph C^1), 137.14 (q, J = 6.12 Hz, Ph C$^{2/6}$), 139.03 (q, J = 6.12 Hz, Ph C^4), 157.09 (s, Im C^2); ^{19}F{^{1}H} NMR (C$_6$D$_6$): δ = -128.3 (quint, 2 F, J = 8.0 Hz, CF$_2$CF_2CF$_2$), -94.9 (t, 4 F, J = 7.7 Hz, CCF_2CF$_2$); MS (EI, 70 eV) m/z (%) 468 (65) (M$^+$), 467 (75) (M$^+$ - H), 449 (15) (M$^+$ - F), 367 (10) (M$^+$ - C$_2$HF$_4$), 148 (100) (C$_{10}$H$_{14}$N$^+$). Anal. Calcd for C$_{25}$H$_{26}$F$_6$N$_2$: C, 64.09; H, 5.59; N, 5.98. Found: C, 63.76; H, 5.82; N, 5.90.

Synthesis of 4. To a solution of 0.102 g (0.33 mmol) of **1** in 30 mL of hexane, 0.120 g (0.57 mmol) of octafluorocyclopentene in 5 mL of toluene were added at room temperature. The color of the mixture turned to yellow immediately. After stirring for 1 hour at room temperature, the solvents were evaporated and **4** was obtained as a crystalline yellow solid. Yield: 0.161 g (94%); mp. 203 - 204 °C (dec); ^{1}H NMR (C$_6$D$_6$): δ = 2.07 (s, 6 H, p-CH$_3$), 2.21 (s, 12 H, o-CH$_3$), 2.94 (s, 4 H, Im H$^{4/5}$), 6.71 (s, 4 H, Ph H$^{3/5}$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = 17.76 (s, o-CH$_3$), 20.92 (s, p-CH$_3$), 50.76 (s, Im C$^{4/5}$), 66.07 (m, C^2-C), 111.0-121.7 (m, CF$_2$), 129.86 (s, Ph C$^{3/5}$), 135.78 (q, Ph C$^{2/6}$), 136.77 (m, Ph C^1), 138.13 (q, Ph C^4), 160.41 (s, Im C^2); ^{13}C{^{19}F} NMR (C$_6$D$_6$) δ = 17.76 (qt, J = 126.97 Hz, J = 2.42 Hz, o-CH$_3$), 20.92 (qt, J = 126.30 Hz, J = 4.31 Hz, p-CH$_3$), 50.77 (t, J = 148.62 Hz, Im C$^{4/5}$), 66.07 (s, C^2-C), 111.51, 118.18 (s, CF$_2$), 129.85 (dm, J = 156.3 Hz, Ph C$^{3/5}$), 135.78 (q, J = 5.5 Hz, Ph C$^{2/6}$), 136.78 (m, Ph C^1), 138.13 (q, J = 6.1 Hz, Ph C^4), 160.41 (s, Im C^2); ^{19}F NMR (C$_6$D$_6$): δ = -135.0 to -134.0 (m, 4 F, CF$_2$CF_2CF$_2$), -92.6 to -92.2 (m, 4 F, CCF_2CF$_2$); MS (EI, 70 eV) m/z (%) 518 (80) (M$^+$), 517 (95) (M$^+$ - H), 499 (55) (M$^+$ - F), 305 (100) (M$^+$ - C$_5$F$_8$), 148 (70) (C$_{10}$H$_{14}$N$^+$). Anal. Calcd for C$_{26}$H$_{26}$F$_8$N$_2$: C, 60.23; H, 5.05; N, 5.40. Found: C, 60.24; H, 5.34; N, 5.27.

Synthesis of 7. Octafluorocyclopentene (0.25 g,1.2 mmol) in 10 mL of toluene was added to a solution of 0.151 g (0.5 mmol) **5** in 5 mL of toluene at room temperature. A slight exotherm was observed. After 10 min. stirring at ambient temperature, the mixture was evaporated to give a nearly colorless solid. Recrystallization from toluene at -20 °C afforded colorless crystal of **7** suitable for X-ray diffraction. Yield: 0.23 g (89%); mp. 199 - 202 °C (dec); ^{1}H NMR (C$_6$D$_6$): δ = 2.04 (s, 18H), 5.61 (s, 2H), 6.68 (s, 4H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = 17.48, 20.98, 57.56 (q, J = 31.7 Hz), 107-123 (m, CF$_2$) 120.08, 129.58, 133.81, 135.58, 139.65, 148.30 (q, J = 4.8 Hz); ^{13}C{^{1}H}

NMR (C$_6$D$_6$) δ = 17.47 (q, J = 127.3 Hz), 20.99 (qt, J = 126.9 Hz, J = 4.4 Hz), 57.48, 111.87, 119.57, 120.12 (m, C^{4,5}), 129.58 (d, J = 159.8 Hz), 133.80 (m, C^{ipso}), 135.58 (q, J = 6.4 Hz), 139.65 (q, J = 6.1 Hz), 148.23 (t, J = 4.6 Hz); ^{19}F NMR (C$_6$D$_6$): δ = -132.4 (quint, 4F, J = 6.5 Hz), -86.63 (quint, 4F, J = 6.5 Hz). Anal. Calcd for C$_{26}$H$_{24}$F$_8$N$_2$: C, 60.46; H, 4.68; N, 5.42. Found: C, 60.44; H, 4.92; N, 5.44.

Isolation of 9. A solution of 0.25 g (1.2 mmol) of octafluorocyclopentene dissolved in 10 mL of toluene was slowly added to a solution of 0.125 g (1.0 mmol) of **6** in 30 mL of toluene at room temperature. Immediately after addition the color changes from clear to yellow-brown accompanied by a moderate evolution of heat. The mixture was stirred for 1 hour at room temperature after which point the volatiles were removed *in vacuo*. ^{1}H and ^{19}F NMR indicate a mixture of compounds, of which, there is one major signal. A single X-ray quality crystal of **9** was obtained from the reaction mixture by crystallization from toluene/hexane.[35]

Synthesis of 13. Tetrakis(trifluoromethyl)allene, **11**, (0.370 g, 1.18 mmol) was placed in 25 mL of cold THF and 0.318 g (0.945 mmol) of solid **10** was added at room temperature upon which the solution color became pale yellow. The reaction was left to stir at room temperature for 4 hours and was indicated as complete by NMR. The volatiles were removed *in vacuo* to afford 0.520 g (0.80 mmol) of crude material. Compound **7** (0.490 g, 0.75 mmol) can be isolated by crystallization from a toluene/hexane mixture. X-ray quality crystals (m.p. 225 °C) are obtained by re-crystallization from THF/hexane. Yield: 0.490 g (79 %); m.p. 218 °C; ^{1}H NMR (THF-d_8): δ = 1.75 (s, 12H), 2.19 (s, 6H), 2.44 (d, 6H, J = 3.0 Hz), 8.01 (s, 2H); ^{13}C{^{1}H} NMR (THF-d_8) δ = 31.38, 36.20, 41.96, 69.24, 84.26, 122.05 (NCH), 125.69 (q, J_{CF} = 272.8 Hz, CF$_3$), 127.05 (q, J_{CF} = 269.5 Hz, CF$_3$), 132.00 (C$_3$C), 142.50 (C^2); ^{19}F NMR (THF-d_8): δ = -48.24 (m, 6F), -56.66 (m, 6F). Anal. Calcd for C$_{30}$H$_{32}$F$_{12}$N$_2$: C, 55.56; H, 4.97; N, 4.32. Found: C, 55.19; H, 5.09; N, 3.98.

Synthesis of 14. In the drybox, a PTFE stoppered glass bomb is charged with 0.50 g (1.5 mmol) of **10** with ~3 mL of THF and a stirbar. The bomb is stoppered, removed from the drybox and degassed on a 0.235 L vacuum manifold. The bomb is then cooled to liquid nitrogen temperature. To this, 116.3 mmHg (1.50 mmol) of bis(trifluoromethyl)ketene, **12**, is condensed into the bomb. The bomb is sealed and thawed. It is then placed in a dry ice/isopropanol bath and maintained at -78 °C. The reaction mixture is periodically shaken to obtain good mixing. A white solid precipitates out of solution. The reaction mixture is taken back into the drybox where more THF is added to the bomb to dissolve all of the solid. The solution is transferred from the bomb to a scintillation vial then placed in a freezer to crystallize. A fluffy white solid crystallizes and is filtered off, yielding 0.126 g [m.p. = 295 – 300 °C (dec)] of material. The filtrate is concentrated, then let stand with the cap loosened, to allow for X-ray quality crystals to form by slow evaporation over 48 h. Yield: 0.596 g (77%); m.p. 218 °C; ^{1}H NMR (THF-d_8): δ = 1.74 (s, 12H), 2.18 (s, 6H), 2.39 (d, 6H, $^2J_{HH}$ = 13.3 Hz), 2.43 (d, 6H, $^2J_{HH}$ = 13.3 Hz), 7.66 (s, 2H); ^{1}H NMR (C$_6$D$_6$): δ = 1.31 (d, 6H, J = 11Hz), 1.40 (d, 6H, J = 11Hz), 1.84 (s, 6H), 2.20 (s, 12H), 6.38 (s, 2H); ^{13}C{1H} NMR (THF-d_8) δ = 31.17, 36.35, 42.59, 65.26, 89.01 (sept, $^2J_{CF}$ = 29.6 Hz), 117.92, 127.04 (q, $^1J_{CF}$ = 268.5 Hz), 128.44 (q, $^1J_{CF}$ = 265.2 Hz), 164.26 (sept, $^3J_{CF}$ = 1.4 Hz), 146.21 (m, NCN); ^{14}N NMR (THF-d_8): δ = -191.77 (br); ^{19}F NMR (THF-d_8): δ = -51.55 (q, 3F, $^4J_{FF}$ = 8.7 Hz), -57.67 (q, 3F, $^4J_{FF}$ = 8.7 Hz); ^{19}F NMR (C$_6$D$_6$): δ = -49.74 (q, 3F, $^4J_{FF}$ = 7.5 Hz), -55.76 (q, 3F, $^4J_{FF}$ = 7.5 Hz). Anal. Calcd for C$_{27}$H$_{32}$F$_6$N$_2$O: C, 63.02; H, 6.27; N, 5.44. Found: C, 62.93; H, 6.50; N, 5.35.

References

1) Kuhn, N.; Bohnen, H.; Kreutzberg, J.; Bläser, D.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1993**, *1993*, 1136-1137.

2) Kuhn, N.; Bohnen, H.; Kratz, T.; Henkel, G. *Liebigs Ann. Chem.* **1993**, 1149-1151.

3) Kuhn, N.; Bohnen, H.; Blaeser, D.; Boese, R. *Chem. Ber.* **1994**, *127*, 1405-1407.

4) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Bohnen, H.; Blaeser, D.; Boese, R. *J. Organomet. Chem.* **1995**, *493*, C14-18.

5) Kuhn, N.; Bohnen, H.; Henkel, G.; Kreutzberg, J. *Z. Naturforsch.* **1996**, *51b*, 1267-1278.

6) Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2053-2064.

7) Quast, H.; Ach, M.; Kindermann, M. K.; Rademacher, P.; Schindler, M. *Chem. Ber.* **1993**, *126*, 503-516.

8) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *119*, 12742-12749.

9) Zeifman, Y. V.; Tyuleneva, V. V.; Knunyants, I. L. *Dokl. Akad. Nauk SSSR* **1971**, *201*, 1359-1362.

10) Baum, K.; Bigelow, S. S.; Nguyen Nghi, V.; Archibald, T. G.; Gilardi, R.; Flippen-Anderson, J. L.; George, C. *J. Org. Chem.* **1992**, *57*, 235-241.

11) Arduengo III, A. J.; Calabrese, J. C.; Marshall, W. J.; Runyon, J. W.; Schiel, C.; Schinnen, C.; Tamm, M.; Uchiyama, Y. *Z. Anorg. Allg. Chem.* **2015**, in press. .DOI: 10.1002/zaac.201500578

12) Schwerdtfeger, W. in *Ullmann's Encyclopedia of Industrial Chemistry,* VCH, Weinheim, Basel, Cambridge, New York, NY, **1988**, vol. A11, p. 360 ff.

13) Chambers, R. D.; Mobbs, R. H. in *Advances in Fluorine Chemistry*, (Eds.: Stacey, M.; Tatlow, J. C.; Sharpe, A. G.), Butterworths, London, **1965**, vol. 4, p. 50.

14) Park, J. D.; McMurtry, R. J.; Adams, J. H. in *Fluorine Chemistry Reviews* (Ed. Tarrant, P.), Dekker, New York, NY, **1968**, vol. 2, p. 55.

15) Bayliff, A. E.; Bryce, M. R.; Chambers, R. D. *J. Chem. Soc., Perkin Trans. 1* **1987**, 763-767.

16) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem.* **1995**, *107*, 1119-1122.

17) Baenziger, N. C.; Foster, B. A.; Howells, M.; Howells, R.; Vander Valk, P.; Burton, D. J. *Acta Cryst.* **1977**, *B33*, 2327-2329.

18) Burton, D. J.; Howells, R. D.; Vander Valk, P. D. *J. Am. Chem. Soc.* **1977**, *99*, 4830-4831.

19) Stockel, R. F.; Megson, F.; Beachem, M. T. *J. Org. Chem.* **1968**, *33*, 4395-4397.

20) Howells, M. A.; Howells, R. D.; Baenziger, N. C.; Burton, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 5366-5370.

21) Burton, D. J.; Shinya, S.; Howells, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 3689-3690.

22) Burton, D. J; Yang, Z.-Y., Qiu, W. *Chem. Rev.*, **1996**, *96(5)*, 1641–1716.

23) Burton, D. J.; Vander Valk, P. D. *J. Fluorine Chem.* **1981**, *18*, 413-416.

24) Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed.* **1997**, *36*, 2162–2187.

25) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027-11028.

26) Arduengo, A. J., III; Craig, H. A.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J.; Schmutzler, R.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523-14534.

27) Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopic Methods in Organic Chemistry*; Georg Thieme Verlag: Stuttgart, New York, 1995.

28) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR-Spektroskopie von Nichtmetallen, Band 4, ^{19}F-NMR Spektroskopie,* Georg Thieme Verlag, Stuttgart, New York, **1994**, p. 29.

29) Crystal data for **2** at -70 °C with Mo Kα radiation: a = 800.0 (1), b = 783.0 (1), c = 3417.1 (7) pm, β = 91.61 (1)°; monoclinic, $P2_1/n$; Z = 4, μ(Mo) = 0.93 cm^{-1}; 1457 unique reflections with $I \geq 2.0\ \sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized using a riding model. The largest residual electron density in the final difference Fourier map was 0.34 e/Å^3 near C^2. The data/parameter ratio was 5.56. The final R factors were R = 0.071 and R_w = 0.045.

30) Crystal data for **3** at -147 °C with Mo Kα radiation: $a = 1867.4\ (1)$, $b = 1584.8\ (1)$, $c = 1661.3\ (1)$ pm, $\beta = 109.43\ (1)°$; monoclinic, $P2_1/n$; $Z = 8$; $\mu(Mo) = 1.07\ cm^{-1}$; 3872 unique reflections with $I \geq 3.0\ \sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized using a riding model. The largest residual electron density in the final difference Fourier map was $0.23\ e/Å^3$ near $H^{48''}$. The data/parameter ratio was 6.45. The final R factors were $R = 0.045$ and $R_w = 0.041$.

31) The asymmetric unit of **3** contains two independent molecules. The structural parameters of only one of the two independent molecules are discussed, but the corresponding parameters for the second molecule in the asymmetric unit are shown in brackets throughout the discussion.

32) Crystal data for **4** at -100 °C with Mo Kα radiation: $a = 1138.3\ (3)$, $b = 1506.6\ (3)$, $c = 1456.8\ (4)$ pm, $\beta = 100.94\ (2)°$; monoclinic, $P2_1/n$; $Z = 4$; $\mu(Mo) = 1.19\ cm^{-1}$; 2830 unique reflections with $I \geq 3.0\ \sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized using a riding model. The largest residual electron density in the final difference Fourier map was $0.21\ e/Å^3$ near $H^{4'}$. The data/parameter ratio was 8.70. The final R factors were $R = 0.043$ and $R_w = 0.041$.

33) Arduengo, A. J., III; Goerlich, J. R.; Davidson, F.; Marshall, W. J. *Z. Naturforsch., B: Chem. Sci.* **1999**, *54*, 1350-1356.

34) Arduengo, A. J., III; Calabrese, J. C.; Cowley, A. H.; Dias, H. V. R.; Goerlich, J. R.; Marshall, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151-2158.

35) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027–4031.

36) The original crystals of **8** that were submitted for X-ray diffraction studies were opaque and diffracted only weakly. After sitting in a vial for several days, smaller crystals grew in between the originals and the glass. The sample and adventitious water probably reacted with silicon in the glass causing it to lose a fluorine atom at C12, forming the double bond C12=C11 and a SiF_5^- counterion (**9**). Crystal data for **9** at -115 °C with Mo Kα radiation: $a = 1128.5\ (2)$, $b = 1857.3\ (3)$, $c = 875.1\ (1)$ pm, $\beta = 112.24\ (1)°$; triclinic, $P1$; $Z = 4$; $\mu(Mo) = 2.60\ cm^{-1}$; 2483 unique reflections with $I \geq 2.0\ \sigma(I)$. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized using a riding model. The Fourier map was $0.70\ e/Å^3$. The data/parameter ratio was 5.10. The final R factors were $R = 0.057$ and $R_w = 0.046$. The crystals first submitted looked opaque.

37) Crystal data for **13** at -100 °C with Mo Kα radiation: $a = 1492.5\ (3)$, $b = 1264.1\ (2)$, $c = 1726.0\ (3)$ pm, $\beta = 125.30\ (1)°$; monoclinic, $P2_1/n$; $Z = 4$; $\mu(Mo) = 1.32\ cm^{-1}$; 3328 unique reflections with $I \geq 3.0\ \sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized using a riding model. The Fourier map was $0.37\ e/Å^3$. The data/parameter ratio was 7.53. The final R factors were $R = 0.050$ and $R_w = 0.053$. The asymmetric unit consists of one carbene derivative co-crystallized with one THF in general positions.

37) Crystal data for **14** at -70 °C with Mo Kα radiation: $a = 3654.0\ (8)$, $b = 1322.4\ (2)$, $c = 2582.6\ (8)$ pm; $\beta = 101.96\ (1)°$; monoclinic, $C2/c$; $Z = 8$; $\mu(Mo) = 1.12\ cm^{-1}$; 2718 unique reflections with $I \geq 3.0\ \sigma(I)$. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on $|F|$. C, F and N atoms were refined with anisotropic thermal parameters. All H atoms were idealized with C-H = 0.95Å. The Fourier map was $0.22\ e/Å^3$. The data/parameter ratio was 4.01. The final R factors were $R = 0.047$ and $R_w = 0.035$. The asymmetric unit consists of two carbene molecules co-crystallized with one half a THF molecule lying on the two-fold.