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A General Route to Perfluoroalkyl- and Trifluorovinyl-Substituted Fischer Carbene Complexes of Tungsten and Chromium – Syntheses, Characterisation and Structures

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Hexacarbonyltungsten and -chromium [$M(CO)_6$; M = W, Cr] react smoothly with perfluoroalkyl (R_f = CF_3, C_2F_5) and trifluorovinyl (R_f = $CF{=}CF_2$) silanes in the presence of equimolar amounts of fluoride ions with exclusive attack of one of the CO ligands to form the corresponding salts, Cat-[$(CO)_5MC(R_f)O$] (Cat = $[Me_4N]^+$, $[Cs(15\text{-crown-}5)_2]^+$) which after methylation represent the first hitherto unknown perfluoroorgano-substituted Fischer carbene complexes, $(CO)_5$-$MC(R_f)(OCH_3)$, of those metals. The methoxy group can be easily replaced by amino functional groups as shown for the corresponding carbonyltungsten compound. The molecular structures of $(CO)_5WC(CF_3)(OCH_3)$ and $(CO)_5WC(CF_3)[N(C_2H_5)_2]$ have been elucidated by XRD measurements.

Introduction

The first Fischer carbene complexes were synthesised in 1964[1] by means of nucleophilic addition of methyl and phenyllithium to one of the CO ligands of hexacarbonyltungsten. During the last half of the century, the utilisation of various lithium reagents and different target metal carbonyls as well as the application of alternative synthetic protocols to obtain carbene complexes keeps this branch of chemistry flourishing.[2] This can be explained by the easy accessibility and remarkable stability of Fischer carbene complexes and the facile generation of these carbene species. It is noteworthy to mention that the search for the synthesis of substituted carbenes is a complex task often solved only with significant difficulties. This is particularly the case for methods of generating perfluoroalkyl-containing carbenes. These reactions proceed mainly at high temperature or under irradiation induced complex transformations of fluorinated organic and elementorganic substrates.[3] As an alternative to these methods, the oxidative addition of perfluoroiodo alkanes to a carbonyliridium complex[4] maybe considered, followed by reduction of one of the products into a bis(trifluoromethyl)carbene transition metal complex.[5] Thus, a general approach for obtaining fluorinated analogues of Fischer carbene complexes is, to the best of our knowledge, unknown. Our findings can become the basis of a principally new development in fluorinated carbenes chemistry.

Within a few decades, the most efficient reagents for the nucleophilic introduction of perfluoroalkyl, -aryl and -vinyl groups into organic and elementorganic molecules were the corresponding perfluoroorgano(trialkyl)silanes. The overwhelming majority of the publications in this area has been devoted to catalytic processes involving fluoride or other hard (in the sense of the HSAB concept) anions as catalysts or reagents for generating highly reactive silicates.[6] Our main activity in recent years has been focused on reactions of perfluoroorgano-silanes in the presence of fluoride sources to generate equivalents of perfluoroorgano anions. As a result of this approach, we were able not only to open access to numerous perfluoroalkyl elementates[7] but, in the course of perfluoroalkylation of organic substrates containing multiple bonds (C=C, C=O, C=S and C=N), we were able to obtain stable salts of fluorinated organic anions which were valuable synthons in further and previously impossible transformations.[8–14]

Herein, we report a new and convenient synthetic method for preparing the first perfluoroalkyl (CF_3, C_2F_5) and trifluorovinyl-containing Fischer carbene complexes on the basis of reactions of tungsten and chromium hexacarbonyls with perfluoroalkyl and trifluorovinylsilanes in the presence of stoichiometric amounts of fluoride ions.

Results and Discussion

It has to be noted that nucleophilic addition of organic lithium reagents to transition metal carbonyl compounds has been comprehensively investigated whereas, to the best

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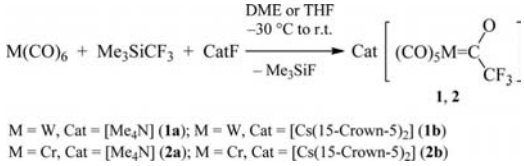
of our knowledge, there are no reports on the interaction of perfluoroalkylating agents with these compounds.

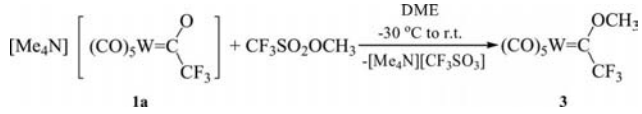
Hexacarbonyltungsten and -chromium react with intermediately formed CF_3^- anions [generated from trimethyl(trifluoromethyl)silane (Me_3SiCF_3) and one fluoride ion equivalent] in DME (dimethoxyethane) or THF at –30 to 25 °C to form the trifluoromethyl-containing salts **1** and **2** in high yields (Scheme 1).



Scheme 1. Synthesis of trifluoromethyl-containing tungsten and chromium salts **1** and **2**.

We succeeded in the isolation of salt **1a** and characterised it by NMR spectroscopic methods. Elemental analyses support the composition. Compound **1a** was obtained as a yellow solid which is stable in dry argon atmosphere at –15 °C for several weeks. The visible onset of decomposition was observed above 95 °C. In solution, this salt is stable at –30 °C in DME and slowly decomposes above 25 °C. Compounds **1b**, **2a** and **2b** were not isolated but their structures unambiguously confirmed by NMR spectroscopic methods.

The generation of salts such as **1a** opens an easy and convenient route to the one-pot synthesis of the first trifluoromethyl-containing tungsten methoxycarbene complex. Methylation of salt **1a** with CF_3SO_2OMe in DME at –30 to 25 °C gave [methoxy(trifluoromethyl)]methylene-pentacarbonyltungsten(0), **3**, in 85% yield (Scheme 2).



Scheme 2. Synthesis of [methoxy(trifluoromethyl)]methylene-pentacarbonyltungsten(0) (**3**).

The carbene complex **3** was isolated as a deep red solid and its composition was elucidated by NMR spectroscopic methods which were supported by a satisfactory elemental analysis. Compound **3** is stable in a dry argon atmosphere at ambient temperature for some days and can be stored for some weeks without any decomposition in a refrigerator. In solution, **3** slowly decomposes above 25 °C in DME and THF. Crystals of the methoxytungsten carbene complex **3** suitable for an X-ray analysis were grown from pentane solution and the molecular structure is depicted in Figure 1.

We next investigated the reactions of the trifluoromethyl-containing methoxycarbene complex **3** with amines [$(C_2H_5)_2$-NH and $C_6H_5CH_2NH_2$] and the system Me_3SiCF_3/[Me_4N]F.

Compound **3** reacts with $(C_2H_5)_2NH$ and $C_6H_5CH_2NH_2$ in DME to selectively form [diethylamino(trifluoromethyl)]-methylene-pentacarbonyltungsten(0) (**4**) and [benzylamino-

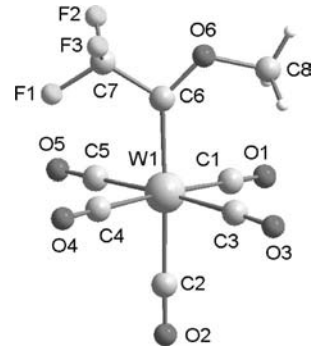
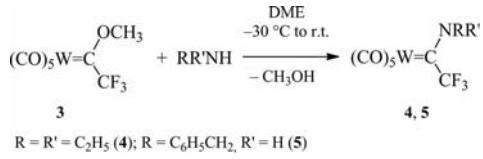


Figure 1. Molecular structure of [methoxy(trifluoromethyl)]methylene-pentacarbonyltungsten(0) (**3**) with the corresponding numbering scheme.

(trifluoromethyl)]methylene-pentacarbonyltungsten(0) (**5**), respectively (Scheme 3). The reactions proceed at –30 to 25 °C to give compounds **4** and **5** in yields of 90–95%.



Scheme 3. Synthesis of [diethylamino(trifluoromethyl)]methylene-pentacarbonyltungsten(0) (**4**) and [benzylamino(trifluoromethyl)]-methylene-pentacarbonyltungsten(0) (**5**).

Both aminocarbene complexes **4** and **5** were isolated as yellow solids and were identified in solution by NMR spectroscopic techniques. Elemental analyses support the compositions. Compounds **4** and **5** are stable in a dry argon atmosphere at –15 °C for several weeks, exhibiting no visible decomposition. In solution, both carbene complexes slowly decomposed above 25 °C. Crystals suitable for an X-ray analysis of **4** were grown from a pentane/hexane mixture at –15 °C. The molecular structure is shown in Figure 2.

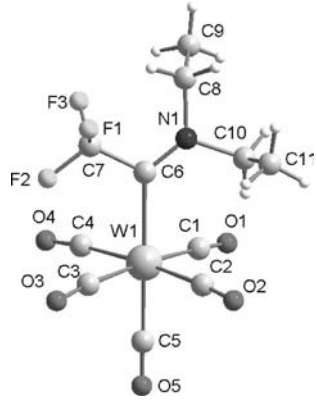


Figure 2. Molecular structure of [diethylamino(trifluoromethyl)]-methylene-pentacarbonyltungsten(0) (**4**) with the corresponding numbering scheme.

Both complexes **3** and **4** essentially display the octahedral coordination adopted by their $M(CO)_6$ synthetic ancestors. The largest deviation from the ideal 180° angles involving *trans*-oriented donor atoms and the central tungsten atom

occurs in the *cis* CO ligands which are bent away from the noncarbonyl ligand in order to accommodate its steric requirements. As expected, this effect is more pronounced in **4** than in **3** due to the bulkiness of the diethylamino group. The electron-withdrawing effect of the trifluoromethyl group exhibits no significant influence on the bonding situation at the carbene site in comparison with the rare number of structurally characterised related alkoxo- and amino-substituted carbene complexes bearing the $W(CO)_5$ moiety. The W–C π bond of **3** with a length of 2.105(7) Å is slightly longer than that found in the related methoxy cyclopentenyl carbene complex, $(CO)_5WC(OCH_3)(C_5H_7)$[15] [2.086(17) Å] but significantly shorter than found for the corresponding methoxy cyclohexenyl derivative, $(CO)_5WC(OCH_3)(C_6H_9)$[16] [2.22(1) Å]. In derivative **4** the W–C bond [2.276(6) Å] is marginally longer than those reported namely $(CO)_5WC(NHCH_3)(C_6H_5)$[17] [2.186(22) Å], $(CO)_5WC(NHCH_3)(C_3H_5)$[18] [2.243(10) Å (*E* isomer); 2.258(9) Å (*Z* isomer)] and $(CO)_5WC[N(CH_3)_2][CH(SCH_3)_2]$[19] [2.255(3) Å] which may be attributed to the greater steric demand of the diethylamino substituent compared with the methyl- and dimethylamino groups in those structurally characterised compounds. While the angle N1–C6–C7 of 113.1(5)° in **4** falls into the range of values reported from 108.2°[18] to 116.4°,[19] the corresponding angle O6–C6–C7 of 100.7(6)° is significantly more acute than in the related compounds [107(1)°;[15] 111.2(13)°[16]]. Crystal data of **3** and **4** are summarised in Tables 1 and 2.

Table 1. Crystal data and structure refinement parameters[a] for $(CO)_5WC(CF_3)(OCH_3)$ (**3**) and $(CO)_5WC(CF_3)[N(C_2H_5)_2]$ (**4**).

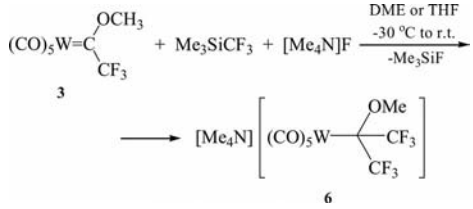
	3	**4**
Empirical formula	$C_8H_3F_3O_6W$	$C_{11}H_{10}F_3N_4O_5W$
M_r (g mol^{-1})	435.95	477.05
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	6.3289(2)	6.4900(2)
b [Å]	7.4062(2)	8.2606(3)
c [Å]	12.5765(4)	13.8813(5)
α [°]	92.796(2)	74.354(2)
β [°]	103.207(2)	89.643(2)
γ [°]	92.273(1)	80.183(2)
Z [Å^3]	2/572.44(3)	2/705.51(4)
θ range [°]	1.67–26.19	2.60–26.89
T [K]	296(2)	296(2)
Index range	$-7 \le h \le 7$	$-7 \le h \le 7$
	$-8 \le k \le 9$	$-10 \le k \le 10$
	$-15 \le l \le 15$	$-16 \le l \le 17$
Total data collected	6058	9081
Unique data	2184	2879
Observed data	2022	2689
R_{merg}	0.0503	0.0539
μ [mm^{-1}]	10.147	8.241
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0368$	$R_1 = 0.0314$
	$wR_2 = 0.0987$	$wR_2 = 0.0710$
R indexes (all data)	$R_1 = 0.0400$	$R_1 = 0.0347$
	$wR_2 = 0.1008$	$wR_2 = 0.0723$
GooF	1.097	1.103

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$, $S_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (0.0591 \cdot P)^2]$ for **1**, and $w = 1/[\sigma^2(F_o)^2 + 2.9294 \cdot P]$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$; $F_c^* = kF_c[1 + 0.001 \cdot |F_c|^2 \lambda^3/\sin(2\theta)]^{-1/4}$.

Table 2. Selected internuclear distances [Å] and angles [°] for $(CO)_5WC(CF_3)(OCH_3)$ (**3**) and $(CO)_5WC(CF_3)[N(C_2H_5)_2]$ (**4**); estimated standard deviations in parentheses.

3		**4**	
W1–C1	2.068(9)	W1–C1	2.058(7)
W1–C2	2.073(8)	W1–C2	2.040(7)
W1–C3	2.055(10)	W1–C3	2.031(7)
W1–C4	2.079(9)	W1–C4	2.065(7)
W1–C5	2.063(10)	W1–C5	2.015(7)
W1–C6	2.105(7)	W1–C6	2.276(6)
O1–C1	1.118(11)	O1–C1	1.129(8)
O2–C2	1.120(10)	O2–C2	1.141(7)
O3–C3	1.139(11)	O3–C3	1.149(8)
O4–C4	1.115(11)	O4–C4	1.127(8)
O5–C5	1.138(12)	O5–C5	1.132(8)
O6–C6	1.315(9)	N1–C6	1.309(8)
O6–C8	1.444(10)	N1–C8	1.498(8)
C6–C7	1.550(11)	N1–C10	1.500(7)
		C6–C7	1.529(8)
C3–W1–C5	176.1(3)	C3–W1–C1	173.6(3)
C1–W1–C4	176.7(3)	C2–W1–C4	175.1(2)
C2–W1–C6	178.0(3)	C5–W1–C6	178.0(2)
C6–O6–C8	120.2(6)	C6–N1–C8	127.9(5)
		C6–N1–C10	121.8(5)
O6–C6–C7	100.7(6)	N1–C6–C7	113.1(5)
O6–C6–W1	134.5(6)	N1–C6–W1	129.2(4)
C7–C6–W1	124.8(6)	C7–C6–W1	117.6(4)

We further investigated the reaction of the methoxycarbene complex **3** and Me_3SiCF_3 in the presence of one $[Me_4N]F$ equivalent. In a similar manner as described for the synthesis of **1a**, the complex **3** reacts with the system $Me_3SiCF_3/[Me_4N]F$ in DME or THF at –30 to 25 °C to form the stable bis(trifluoromethyl)-containing tungsten salt **6** in 70% yield (Scheme 4).

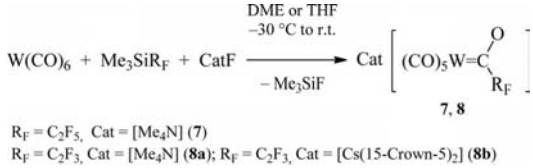


Scheme 4. Reaction of compound **3** with the system $Me_3SiCF_3/[Me_4N]F$.

Whereas the diaryl analogues are stable up to –60 °C,[20] we succeeded in the isolation of salt **6** and were able to characterise it by NMR spectroscopic techniques and elemental analysis. The tungsten compound **6** was obtained as a yellow solid which is stable in a dry argon atmosphere at –15 °C for some days. Visible onset of decomposition was observed above 105 °C.

In order to extend these reactions to derivatives of other fluorine-containing tungsten carbene complexes, we investigated the possibility of synthesising so far unknown pentafluoroethyl and trifluorovinyl-containing tungsten salts. We found that hexacarbonyltungsten reacts with trimethyl(pentafluorethyl)- and trimethyl(trifluorovinyl)silanes,

$Me_3SiC_2F_5$ and $Me_3SiCF{=}CF_2$, in the presence of fluoride ions under above mentioned conditions to form the salts **7** and **8**, respectively (Scheme 5).



Scheme 5. Preparation of the salts **7** and **8**.

Compounds **7** and **8** were detected in the ^{19}F NMR spectra and may be used for the preparation of the corresponding Fisher carbene complexes which will be the subject of further investigations.

Conclusions

In summary, a new, convenient and efficient synthesis of the first perfluoroalkyl- and trifluorovinyl-containing salts of tungsten and chromium has been developed by means of the direct addition of perfluoroalkyl (CF_3, C_2F_5) and trifluorovinyl groups, generated from the corresponding fluoroorgano(trimethyl)silanes in the presence of 1 equiv. of fluoride ion source to hexacarbonyltungsten and -chromium. The formation of salts such as **1a** opens an easy and convenient route to the synthesis of the first representatives of hitherto unknown trifluoromethyl-containing tungsten methoxy- **3** and aminocarbene **4**, **5** complexes. It should also be noted that the reaction of **3** and Me_3SiCF_3 in the presence of $[Me_4N]F$ proceeds selectively to yield the stable bis(trifluoromethyl)-containing tungsten salt **6** which was isolated and unambiguously identified.

Experimental Section

General: All experiments were carried out in a dry argon atmosphere in carefully dried reaction vessels using Schlenk techniques. Solvents were purified by reported methods.[21] $[Me_4N]F$,[22] $Me_3SiCF{=}CF_2$[23] and $Me_3SiC_2F_5$[24] were synthesised following literature procedures. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on Varian VXR 300 (299.9 MHz, ^1H), Varian GEMINI 200 (188.1 MHz, ^{19}F) and Bruker AVANCE 400 (100.6 MHz, ^{13}C) spectrometers, respectively. Chemical shifts are given in ppm relative to Me_4Si (^1H, ^{13}C) and CCl_3F (^{19}F) as external standards. IR spectra were recorded on a VERTER 70 spectrometer in the solvent specified. C, H and N analyses were carried out in the analytical laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Melting points were measured on an electro-thermal apparatus and are uncorrected.

Single Crystal X-ray Diffraction Study: Single crystals of $(CO)_5WC(CF_3)(OCH_3)$ **3** and $(CO)_5WC(CF_3)[N(C_2H_5)_2]$ **4** were obtained upon cooling pentane and pentane/hexane solutions, respectively, to approximately –15 °C for several weeks. Data collections for X-ray crystal structure determination were performed on a Bruker Smart Apex II diffractometer (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS-97.[25] The refinement and all further calculations were carried out using SHELXL-97.[26] The nonhydrogen atoms were refined anisotropically, using weighted full-matrix least-squares of F^2. For **3**, the hydrogen atoms were located and refined isotropically, while for **4** the hydrogen atoms were added geometrically (placed at calculated position).

CCDC-802145 (for **3**) and -802146 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of the Salts 1, 2, 7 and 8: To a well stirred suspension of hexacarbonyltungsten or -chromium $[M(CO)_6$; M = W, Cr] (7.96 mmol) and CatF [Cat = $(Me_4N)^+$ or Cs^+ with 15-crown-5 (19.10 mmol)] (9.55 mmol) in dry dimethoxyethane (40 mL) at –30 ± 5 °C, was added Me_3SiR_f (R_f = CF_3, C_2F_5 or $CF{=}CF_2$) (11.14 mmol) dropwise over a period of 30 min. The mixtures were stirred for 30 min at –30 ± 5 °C and for 1 h at room temperature. The formation of the salts **1**, **2**, **7** and **8** was monitored by NMR spectroscopic means. In the case of **1a**, insoluble impurities were filtered off in a dry argon atmosphere; all volatile components were removed in vacuo giving a yellow solid.

1a: Yield 96% (3.78 g, 7.64 mmol); m.p. (onset of decomposition) 97 °C (glass capillary). ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.32 (s, 12 H, $[Me_4N]^+$) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –83.2 [s, $^1J_{F,C}$ = 309, $^2J_{F,C}$ = 29 Hz, 3 F, CF_3] ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]THF, 22 °C): δ = 118.4 (q, $^1J_{F,C}$ = 309, $^2J_{W,C}$ = 20 Hz, CF_3), 254.6 (q, $^1J_{W,C}$ = 93, $^2J_{F,C}$ = 29 Hz, CF_3CO), 201.0 (s, $^1J_{W,C}$ = 127 Hz, CO_{eq}), 205.7 (s, $^1J_{W,C}$ = 134 Hz, CO_{ax}), 55.3 ("t", $^1J_{C,N}$ = 4 Hz, $[Me_4N]^+$) ppm. IR (nujol): $\tilde{\nu}$ = 2060 [s, ν(CO)], 1980 (vs(CO), 1848 [br.vs, (CO)], 1000 [s, ν(C–O)], 1214 [s, $\nu(CF_3)$], 1104 [s, $\nu(CF_3)$] cm^{-1}. Analytical data $C_{11}H_{12}F_3NO_6W$ (495.08): calcd. C 26.69, H 2.44, N 2.83; found C 27.39, H 2.81, N 2.94

1b: ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.62 (s, 40 H, CH_2-crown) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –83.3 (s, $^1J_{F,C}$ = 309, $^2J_{F,C}$ = 29 Hz, 3 F, CF_3) ppm.

2a: ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.38 (s, 12 H, $[Me_4N]^+$) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –82.8 (s, $^1J_{F,C}$ = 311, $^2J_{F,C}$ = 28 Hz, 3 F, CF_3) ppm.

2b: ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.62 (s, 40 H, CH_2-crown) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –82.3 (s, $^1J_{F,C}$ = 311, $^2J_{F,C}$ = 28 Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]THF, 22 °C): δ = 115.6 (q, $^1J_{F,C}$ = 311 Hz, CF_3), 268.8 (q, $^2J_{F,C}$ = 28 Hz, CF_3CO), 220.6 (s, CO_{eq}), 225.8 (s, CO_{ax}), 69.4 (s, C-crown) ppm.

7: ^{19}F NMR (188.1 MHz, DME, 22 °C): δ = –79.6 (s, 3 F, CF_3), –116.5 (s, 2 F, CF_2) ppm.

8a: ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.32 (s, 12 H, $[Me_4N]^+$) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –109.7 (dd, $^2J_{F,F}$ = 37, $^3J_{F,Fcis}$ = 31 Hz, 1 F, $=CF_2$), –113.3 (dd, $^2J_{F,F}$ = 37, $^3J_{F,Ftrans}$ = 111 Hz, 1 F, $=CF_2$), –159.8 (dd, $^3J_{F,Ftrans}$ = 111, $^3J_{F,Fcis}$ = 31 Hz, 1 F, =CF) ppm. **8b**: ^1H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.72 (s, 40 H, CH_2-crown) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –110.9 (dd, $^2J_{F,F}$ = 38, $^3J_{F,Fcis}$ = 30 Hz, 1 F, $=CF_2$), –114.0 (dd, $^2J_{F,F}$ = 38, $^3J_{F,Ftrans}$ = 111 Hz, 1 F, $=CF_2$), –160.4 (dd, $^3J_{F,Ftrans}$ = 111, $^3J_{F,Fcis}$ = 30 Hz, 1 F, =CF) ppm.

[Methoxy(trifluoromethyl)]methylene-pentacarbonyltungsten(0) 3: To a solution of **1a** (0.56 g, 1.13 mmol) in dry dimethoxyethane (10 mL) at –30 °C, was added CF_3SO_2OMe (0.24 g, 1.47 mmol). The reaction mixture was allowed to reach room temperature and stirred for 1 h. All volatile components were removed in vacuo and

the product was extracted into pentane. The precipitated $[Me_4N][CF_3SO_3]$ was filtered under a dry argon atmosphere and the solvent was evaporated in vacuo. The residue was purified by sublimation (0.04 Torr, 40–45 °C) to yield 86% (0.42 g, 0.97 mmol) as a deep red solid; m.p. 53–54 °C (glass capillary). ^{1}H NMR (299.9 MHz, CD_2Cl_2, 22 °C): δ = 4.64 (s, 3 H, CH_3) ppm. ^{19}F NMR (188.1 MHz, CD_2Cl_2, 22 °C): δ = –71.4 (s, $^1J_{F,C}$ = 287, $^2J_{F,C}$ = 30 Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 22 °C): δ = 69.3 (s, OCH_3), 121.7 (q, $^1J_{F,C}$ = 287 Hz, CF_3), 295.9 (q, $^2J_{F,C}$ = 30 Hz, CF_3CO), 194.2 (s, $^1J_{W,C}$ = 127 Hz, CO_{eq}), 201.7 (s, $^1J_{W,C}$ = 125 Hz, CO_{ax}) ppm. IR (CCl_4): $\tilde{\nu}$ = 2098 [s, ν(CO)], 2087 [s, ν(CO)], 2007 [vs, ν(CO)], 1981 [s, ν(CO)], 1964 [vs, ν(CO)], 995 [s, ν(C–O)], 1154 [s, $\nu(CF_3)$], 1129 [s , $\nu(CF_3)$], 1203 [s, $\nu(CF_3)$], 1149 [s, $\nu(CF_3)$], 2956, [vvw, ν(CH)] cm^{-1}. Analytical data $C_8H_3F_3O_6W$ (435.95): calcd. C 22.04, H 0.69; found C 22.31, H 0.78.

Synthesis of [Diethylamino(trifluoromethyl)]methylene-pentacarbonyltungsten(0) 4 and [Benzylamino(trifluoromethyl)]methylene-pentacarbonyltungsten(0) 5: To a solution of **3** (1.31 g, 3 mmol) in dry dimethoxyethane (10 mL) at –30 °C was added (3 mmol) RR′NH (R = R′ = C_2H_5 or R = CH_2Ph, R′ = H). The reaction mixture was allowed to reach room temperature and stirred for 1 h. All volatile components were removed in vacuo to obtain **4** or **5**, as yellow solids. The compounds **4** and **5** were purified by sublimation (0.04 Torr, 75 °C).

4: Yield 95% (1.36 g, 2.85 mmol); m.p. 97–98 °C (glass capillary). ^{1}H NMR (299.9 MHz, CD_2Cl_2, 22 °C): δ = 1.34 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 1.41 (t, $^3J_{H,H}$ = 7 Hz, 3 H, CH_3), 3.85 (q, $^3J_{H,H}$ = 7 Hz, 2 H, CH_2), 4.35 (q, $^3J_{H,H}$ = 7 Hz, 2 H, CH_2) ppm. ^{19}F NMR (188.1 MHz, CD_2Cl_2, 22 °C): δ = –58.1 (s, $^1J_{F,C}$ = 285, $^2J_{F,C}$ = 32 Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]THF, 22 °C): δ = 15.32 (s, CH_3), 15.62 (s, CH_3), 53.5 (q, $^4J_{F,C}$ = 4 Hz, CH_2), 62.2 (s, CH_2), 124.8 (q, $^1J_{F,C}$ = 285 Hz, CF_3), 238.4 (q, $^2J_{F,C}$ = 32 Hz, CF_3C), 198.2 (q, $^1J_{W,C}$ = 127 Hz, CO_{eq}), 203.5 (s, $^1J_{W,C}$ = 125 Hz, CO_{ax}) ppm. IR (CCl_4): $\tilde{\nu}$ = 2073 [s, (CO)], 1981 [s, (CO)], 1945 [vs, (CO)], 1933 [vs, (CO)], 1229 [m, $\nu(CF_3)$], 1204 [m, $\nu(CF_3)$], 1157 [m, $\nu(CF_3)$], 1121 [m, $\nu(CF_3)$], 2982 [vvw, ν(CH)] cm^{-1}. Analytical data $C_{11}H_{10}F_3NO_5W$ (477.05): calcd. C 27.70, H 2.11, N 2.94; found C 27.98, H 2.37, N 3.01.

5: Yield 92% (1.41 g, 2.76 mmol); m.p. 94–96 °C (glass capillary). ^{1}H NMR (299.9 MHz, CD_2Cl_2, 22 °C): δ = 5.11 (s, 2 H, CH_2), 7.31–7.35 (m, 2 H, C_6H_5), 7.40–7.51 (m, 3 H, C_6H_5) ppm. ^{19}F NMR (188.1 MHz, CD_2Cl_2, 22 °C): δ = –68.7 (s, $^1J_{F,C}$ = 282, $^2J_{F,C}$ = 35 Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 22 °C): δ = 59.0 (s, CH_2), 123.1 (q, $^1J_{F,C}$ = 282 Hz, CF_3), 127.9 (s, C-3,5), 128.8 (s, C-4), 128.9 (s, C-2,6), 131.8 (s, C-1), 237.4 (q, $^2J_{F,C}$ = 35 Hz, CF_3C), 195.6 (s, $^1J_{W,C}$ = 127 Hz, CO_{eq}), 200.9 (s, $^1J_{W,C}$ = 124 Hz, CO_{ax}) ppm. IR (CCl_4): $\tilde{\nu}$ = 2073 [s, (CO)], 1988 [s, (CO)], 1964 [sh.vs, (CO)], 1940 [vs, (CO)], 1242 [m, $\nu(CF_3)$], 1180 [m, $\nu(CF_3)$], 1053 [m, $\nu(CF_3)$], 3035 [vvw, $\nu(CH_{Ph})$], 3310 [vvw, ν(NH)] cm^{-1}. Analytical data $C_{14}H_8F_3NO_5W$ (511.08): calcd. C 32.90, H 1.58, N 2.74; found C 33.18, H 1.79, N 2.81.

Salt 6: To a well stirred mixture of **3** (1.31 g, 3 mmol) and $[Me_4N]F$ (0.35 g, 3.75 mmol) in dry dimethoxyethane (30 mL) at –30 ± 5 °C, was added Me_3SiCF_3 (0.59 g, 4.13 mmol) dropwise over a period of 30 min. The mixture was stirred for 1 h at –30 ± 5 °C and for 2 h at room temperature. All volatile components were removed in vacuo and the product was extracted into dichloromethane. Insoluble impurities were filtered under a dry argon atmosphere and the solvent was evaporated in vacuo to give a yellow solid in 77% yield (1.34 g, 2.31 mmol); m.p. (onset of decomposition) 105 °C (glass capillary). ^{1}H NMR (299.9 MHz, [D$_8$]THF, 22 °C): δ = 3.56 (q, $^5J_{F,H}$ = 0.9 Hz, 3 H, OCH_3), 3.33 (s, 12 H, $[Me_4N]^+$) ppm. ^{19}F NMR (188.1 MHz, [D$_8$]THF, 22 °C): δ = –62.2 (s, $^1J_{F,C}$ = 283, $^2J_{F,C}$ = 35 Hz, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D$_8$]THF, 22 °C): δ = 58.8 (s, OCH_3), 88.1 [sept, $^2J_{F,C}$ = 35 Hz, $(CF_3)_2CO$], 131.2 (qq, $^1J_{F,C}$ = 283, $^3J_{F,C}$ = 6 Hz, CF_3), 202.3 (s, $^1J_{W,C}$ = 127 Hz, CO_{eq}), 204.4 (s, $^1J_{W,C}$ = 135 Hz, CO_{ax}), 55.8 ("t", $^1J_{C,N}$ = 4 Hz, $[Me_4N]^+$) ppm. IR (nujol): $\tilde{\nu}$ = 2060 [s, (CO)], 1980 [vs, (CO)], 1900 [br.vs, [CO]], 948 [s, ν[C–O]], 1229 [s, $\nu[CF_3]$] 1184 [s, $\nu(CF_3)$], 1131 [s, $\nu(CF_3)$], 1091 (s) cm^{-1}. Analytical data $C_{13}H_{15}F_6NO_6W$ (579.12): calcd. C 27.73, H 2.69, N 2.49; found C 28.51, H 2.98, N 2.54.

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