ELECTRONIC SUPPORTING INFORMATION

An Unusual Alkylidyne Homologation

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Experimental Procedures

General Considerations

All manipulations of air-sensitive compounds were carried out at room temperature under a dry oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, or inert atmosphere (argon) glovebox techniques with dried and degassed solvents. NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C at 100.5 MHZ, ^{31}P at 162.0 MHz), Bruker Avance 700 (^{1}H at 700.1 MHz, ^{13}C at 176.1 MHz, ^{31}P at 283.5 MHz), or Bruker Avance 800 with cryoprobe (^{1}H at 800.1 MHz, ^{13}C at 200.2 MHz) spectrometer. Chemicals shifts (δ) are reported in ppm and referenced to the solvent peak (^{1}H, ^{13}C) or external 85% H_3PO_4. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), sep (septet), m (multiplet), and combinations thereof for more highly coupled systems and $^nJ_{ab}$ reported in Hz. Whilst ^{13}C{^{1}H} for carbon nuclei of the $(C_6H_{11})_2P(CH_2CH_2)P(C_6H_{11})_2$ ligand were observed, their narrow spectral range precluded unequivocal assignment for the dcpe carbon environments. Similarly, proton environments within the dcpe ligand could not be uniquely identified due to the complex multiplicities and similar chemical shifts encountered. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalysis has been performed at the London Metropolitan University. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix. Data for X-ray crystallography were collected on either an Oxford Diffraction SuperNova or Oxford Diffraction Xcalibur diffractometer. The synthesis of the complex [W(≡CH)Br(CO)$_2$(dcpe)] (**1**) has been described previously.[1]

Synthesis of W(≡C^{t}Bu)(SiCl$_3$)(CO)$_2$(dcpe) 3

To a yellow solution of W(CH)(Br)(dcpe)(CO)$_2$ (**1**: 151 mg, 0.200 mmol) in THF (10 mL) at -78°C (dry ice/acetone), 0.38 mL of a 1.6 M solution of ^{t}BuLi in hexanes (0.60 mmol) was added *via* syringe. The resultant dark red solution was allowed to stir for 30 minutes at -78°C before 0.22 mL of a 1.0 M solution of $SiCl_4$ (0.22 mmol) in THF was added *via* syringe. The reaction was allowed to stir at -78°C for a further 30 minutes before removal of the cooling bath. THF was removed *in vacuo* and the product was extracted using DCM (2x 10mL) *via* filtration through a glass frit from the insoluble LiBr precipitate. The DCM was removed *in vacuo* and resultant crude product was washed with benzene (2 x 5mL) to afford a crude light yellow powder. Recrystallisation from DCM/hexane afforded **7** as bright yellow crystals. Yield 64 mg, 37%. IR (CH_2Cl_2) ν/cm^{-1}: 1990 (CO), 1921 (CO). IR (Nujol) ν/cm^{-1}: 1978 (CO), 1911 (CO). ^1H NMR (CD_2Cl_2, -40°C): δ_H 2.09 (m, 2 H, dcpe), 2.01-1.87 (m, 4 H, dcpe), 1.79-1.04 (m, 42 H, dcpe), 1.30 (s, 9 H, $C(C\mathbf{H_3})_3$). ^{13}C NMR (C_6D_6, 25°C): δ_C 324.0 ($W{\equiv}\underline{\mathbf{C}}$, observed through HMBC in C_6D_6, carbonyl resonance not observed), 54.2 pm ($\underline{\mathbf{C}}(CH_3)_3$), 41.0 (d, $^1J_{CP}$ = 21.2 Hz, $\underline{\mathbf{C}}H[C_6H_{11}]$), 38.9 (d, $^1J_{CP}$ = 21.3 Hz), 31.8 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.8 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 30.4 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 29.0 (d, J_{CP} = 3.9, $\underline{\mathbf{C}}H_2[C_6H_{11}]$), 28.9 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 27.8 ($\underline{\mathbf{C}}(CH_3)_3$), 27.6-27.2 (m, 3x$\underline{\mathbf{C}}H_2[C_6H_{11}]$) 26.2 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 26.0 ($\underline{\mathbf{C}}H_2[C_6H_{11}]$), 22.1 (dd, $^1J_{CP}$ = 22.9, $^2J_{CP}$ = 13.2, $P(\underline{\mathbf{C}}H_2)_2P$). $^{31}P\{1H\}$ NMR (CD_2Cl_2, -40 °C): δ_P 49.3 ($^1J_{PW}$ **=** 216.1). MS-ESI: 864.2173 $[M]^+$. Accurate mass: found 864.2173 $[M]^+$. Calcd for $C_{33}H_{57}O_2SiP_2Cl_3W$ 864.2178. Anal. found: C, 44.58; H, 7.17; N, 0.00%. Calcd. for $C_{33}H_{57}O_2SiP_2Cl_3W$: C, 45.77; H, 6.63; N, 0.00% (Hydrolytic and thermal sensitivity likely saw decomposition of sample *en route* to London Metropolitan University). Crystals suitable for crystallographic analysis were obtained *via* layering hexane over a solution of **4** in DCM at -20°C

Attempted Synthesis of W(≡C^{t}Bu)($SiMe_3$)$(CO)_2$(dcpe) and observation of W(CH^{t}Bu)(η^2-Cl,Si-$SiCl_4$)$(CO)_2$(dcpe)

The above procedure was conducted, unsuccessfully, using excess $ClSiMe_3$ in place of $SiCl_4$. On one occasion, which was not successfully reproduced, attempts to crystallise the crude product provided a small number of red crystals identified as a chloroform solvate of the tetrachlorosilane complex W(=CH^{t}Bu)(η^2-Cl,Si-$SiCl_4$)$(CO)_2$(dcpe) **8**.

Crystal data for $C_{33}H_{58.7}Cl_{3.3}O_2P_2SiW{\cdot}CHCl_3$ (**8**)

M_w = 997.73, monoclinic, $P2_1/c$, a = 10.9285(2) Å, b = 19.4442(4) Å, c = 20.0693(5) Å, β = 98.632(2)°, V = 4216.35(17) Å^3, Z = 4, ρ_{calcd} = 1.572 Mg m^{-3}, μ(Cu Kα) = 9.966 mm^{-1}, T = 150(1) K, red plate, 0.104 × 0.055 × 0.019 mm, 8184 independent reactions, F^2 refinement, R = 0.037, wR = 0.097 for 6702 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 143.6°), 427 parameters, 0 restraints (CCDC 1557985).

Discussion of the Crystal Structure of **8**

The 7-coordinate tungsten may be described as an octahedron with the Cl1···C2···C3 face capped by the $SiCl_3$ ligand. The neopentylidene ligand has a W1–C1–C6 angle of 142.0(4)° which given the coordinative saturation at tungsten may be attributed to steric pressures rather than any incipient α-agostic interaction. The W=C bond length (2.010(6) Å) is somewhat long for a tungsten neopentylidene however it should be noted that data are otherwise unavailable for 7-coordinate complexes. Lower coordination geometries, *e.g.,* octahedral tungsten have shorter W–C separations (1.859–1.986 Å) invariably accompanied by α-agostic C–H–W interactions.[2] Of note however is the geometry at silicon, which departs significantly from conventional tetrahedral hybridisation. This distortion (silicon angle sum for W1, Cl2 and Cl3 = 340.8°) is best understood in terms of a weak inter-ligand hypervalent interaction between the tungsten-bound chloride (Cl1) and the silicon (Cl1···Si1 = 2.862 Å), which from this perspective begins to approach trigonal bipyramidal coordination.[3] The coordination of intact tin halides to zerovalent group 6 metal centres without Sn–Cl bond rupture is well-established, *e.g.,* [W($SnCl_4$)$(CO)_3$(COD)],[4] however this type of interaction, effectively an intercepted Si–C oxidative addition, has not been previously documented for silicon halides and remains rare for germanium halides**.**

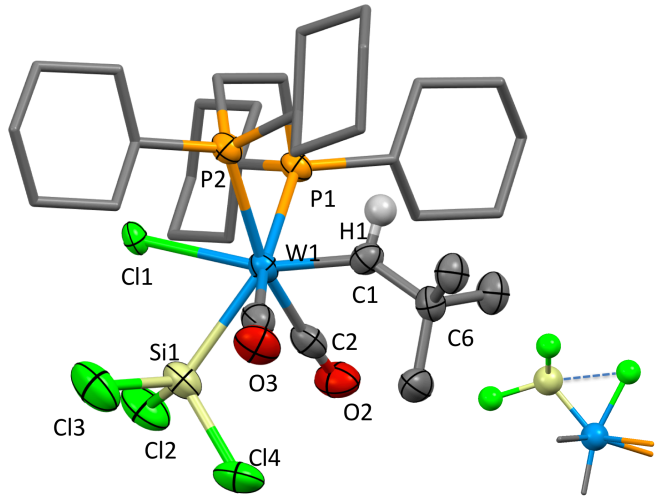

Figure ESI-1. Molecular structure of **8** in a crystal of **8**.$CHCl_3$ (60% displacement ellipsoids, most H-atoms omitted, cyclohexyl groups simplified). Selected bond lengths (Å) and angles: W1–Cl1 2.5847(9), W1–P1 2.6488(9), W1–P2 2.6236(10), W1–Si1 2.5799(12), W1–C1 2.006(4), C6–C1–W1 142.0(3), Cl2–Si1 2.054(2), Cl3–Si1 2.025(3), Cl4–Si1 2.1411(19), Si1···Cl1 2.863 (Σr_{cov} = 2.13, Σr_{vdW} = 3.55). Inset = View normal to Cl2···Cl3 vector.

Crystal data for $C_{33}H_{57}O_2SiP_2Cl_3W$ (**3**)

M_w = 866.01, triclinic, P-1, a = 13.3178(2)Å, b = 16.6846(3) Å, c = 18.1264(3) Å, α = 99.3043(14)°, β = 95.4402(14)°, γ = 106.7416(16)°, V = 3763.42(12) Å^3, Z = 4, ρ_{calcd} = 1.528 Mg m^{-3}, μ(Cu Kα) = 8.967 mm^{-1}, T = 150(1) K, yellow block, 15176 independent reactions, F^2 refinement, R = 0.031, wR = 0.067 for 13046 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 147.9°), 763 parameters, 0 restraints (CCDC 1557986).

Crystal data for $C_{32}H_{59}Cl_3P_2W$ (**4**)

M_w = 795.93, orthorhombic, *P*bca, *a* = 14.7156(4) Å, *b* = 23.4584(6) Å, *c* = 23.8845(7) Å, *V* = 8245.0(4) Å^3, Z = 8, ρ_{calcd} = 1.282 Mg m^{-3}, μ(Cu Kα) = 7.83 mm^{-1}, *T* = 150(1) K, brown block, 0.090 × 0.076 × 0.031 mm, 8039 independent reactions, F^2 refinement, *R* = 0.053, *wR* = 0.122 for 5937 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 143.4°), 359 parameters, 66 restraints (CCDC 1587450).

Crystal data for $C_{26}H_{48}Cl_3OP_2W.CHCl_3$ (6)

M_w = 848.15, orthorhombic, $P2_12_12_1$, *a* = 12.31677(14) Å, *b* = 14.9414(3) Å, *c* = 18.7844(3) Å, *V* = 3456.89(10) Å^3, *Z* = 4, ρ_{calcd} = 1.630 Mg m^{-3}, μ = 11.486 mm^{-1}, *T* = 150(2) K, yellow block, 0.227 × 0.081 × 0.064 mm, 6981 independent reactions, F^2 refinement, *R* = 0.050, *wR* = 0.119 for 6703 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 148°), 418 parameters, 84 restraints (CCDC 1557986).

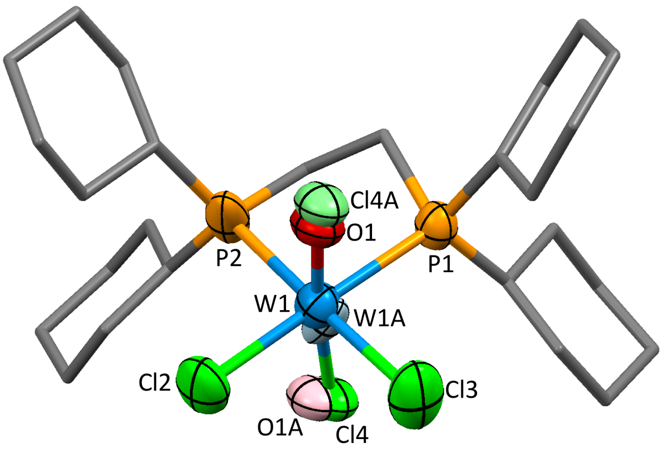

Figure ESI-2. Molecular structure of **6** in a crystal of **6**.$CHCl_3$ (60% displacement ellipsoids, H-atoms omitted, cyclohexyl groups simplified). Minor component (occupancy 0.254(9), designated 'A') of the O1=W1-Cl4 triatomic unit depicted in pastel shades. W1–Cl4 2.438(9), W1–P1 2.585(3), W1–P2 2.533(4), W1–Cl2 2.343(4), W1–Cl3 2.403(4), W1=O1 1.806(14).

In addition to one cyclohexyl ring showing positional disorder, the O1=W1-Cl4 spine displays disorder with the inverted triatomic based on O1A=W1A-Cl4A with occupancies for he two units refining to 0.746(9):0.254(9).

Computational Analysis of $(Cl_3Si)(CO)_2(dmpe)W{\equiv}CH$

Table ESI-1. Comparison of Geometric and Spectroscopic Data

	$Cl_3Si(CO)_2(dcpe)W{\equiv}C^tB$ (Measured)^a	$Cl_3Si(CO)_2(dmpe)W{\equiv}CH$ (Calculated)
W≡CH/Å	1.834(3), 1.833(4)	1.823
W–CO/Å	2.013(3), 2.023(4) 2.015(4), 2.018(4)	2.013, 2.013
W–Si/Å	2.6880(9), 2.6887(9)	2.753
W–P/Å	2.5473(8), 2.5590(8) 2.5618(8), 2.5544(8)	2.612, 2.615
P–W–P/°	78.78(3), 79.26(3)	79.24
νCO/cm^{-1}	1990, 1921	1983, 1929
νWC/cm^{-1}	-	954 vw

^{a}Two crystallographically independent molecules

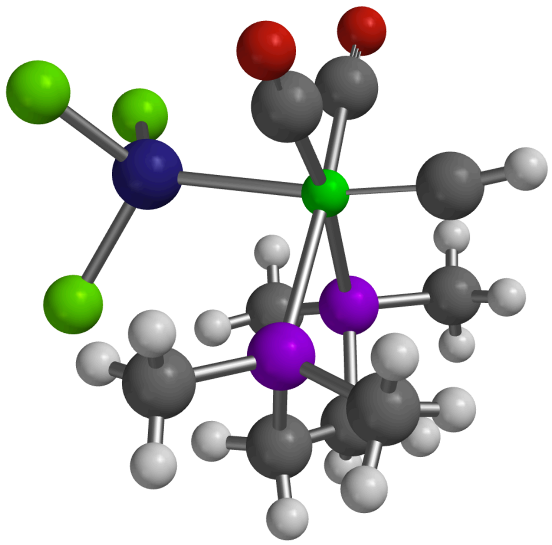

Figure ESI-3. Optimised Geometry for $(Cl_3Si)(CO)_2(dmpe)W{\equiv}CH$

Table ESI-2 Standard Nuclear Orientation (Å) for $Cl_3Si(CO)_2(dmpe)W{\equiv}CH$ (Geometry Optimisation at DFT: B3LYP-LANL2DZ).

	Atom	X	Y	Z
1	W1	-1.0418998	0.8705173	0.8747805
2	C1	-2.7242001	0.3852115	0.3686689
3	H3	-3.7846909	0.2021168	0.1866551
4	P1	0.0499366	0.8856024	-1.4977061
5	P2	-0.0047047	-1.5288803	0.7991561
6	C2	-1.5896406	2.8049209	0.7650141
7	O1	-1.9611688	3.9154066	0.6667306
8	C3	-1.6182070	0.6950330	2.7955691
9	O2	-2.0091154	0.5640302	3.8961624
10	Si1	1.2996704	1.8381941	1.9526223
11	Cl1	1.5689420	4.0330462	2.1007919
12	Cl2	3.2030915	1.2448209	0.8451282
13	Cl3	1.7842219	1.1323491	4.0094729
14	C4	1.1158455	-0.6903563	-1.7085560
15	H2	2.0976610	-0.4688939	-1.2782996
16	H1	1.2518980	-0.8809816	-2.7796946
17	C5	-1.2199159	0.7211404	-2.8837169
18	H5	-1.8187936	-0.1769901	-2.7191898
19	H8	-0.7220925	0.6639785	-3.8563389
20	H11	-1.8834207	1.5886765	-2.8623219
21	C6	0.4695843	-1.9000126	-1.0200679
22	H12	-0.4577173	-2.1870572	-1.5293361
23	H13	1.1432436	-2.7644454	-1.0401857
24	C7	-1.1923939	-2.9300544	1.2196758
25	H9	-2.1049069	-2.8163274	0.6309454
26	H14	-1.4493547	-2.8693148	2.2801230
27	H15	-0.7314975	-3.9008950	1.0141599
28	C8	1.5351600	-2.0087131	1.7726003
29	H10	2.3700784	-1.3679513	1.4835195
30	H16	1.7865927	-3.0563878	1.5819919
31	H17	1.3463963	-1.8625500	2.8384868
32	C9	1.1626862	2.2633109	-2.1359375
33	H7	2.0187778	2.3762722	-1.4687951
34	H18	0.5980656	3.1985937	-2.1567364
35	H19	1.5118684	2.0265900	-3.1453723

References

1 A. F. Hill, J. S. Ward and Y. Xiong, *Organometallics*, 2015, **34**, 5057–5064.

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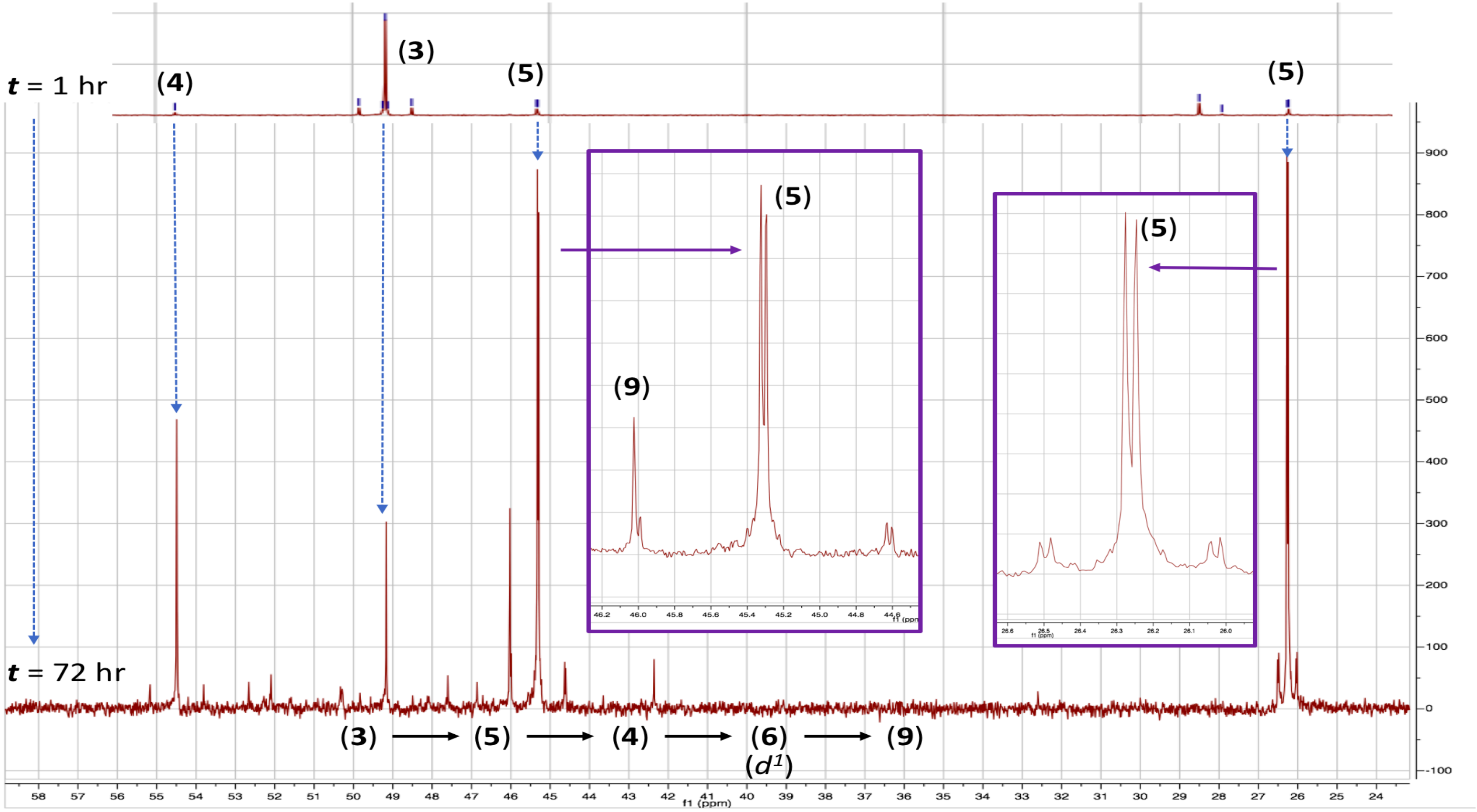
4 M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268–1273.

Selected Spectra

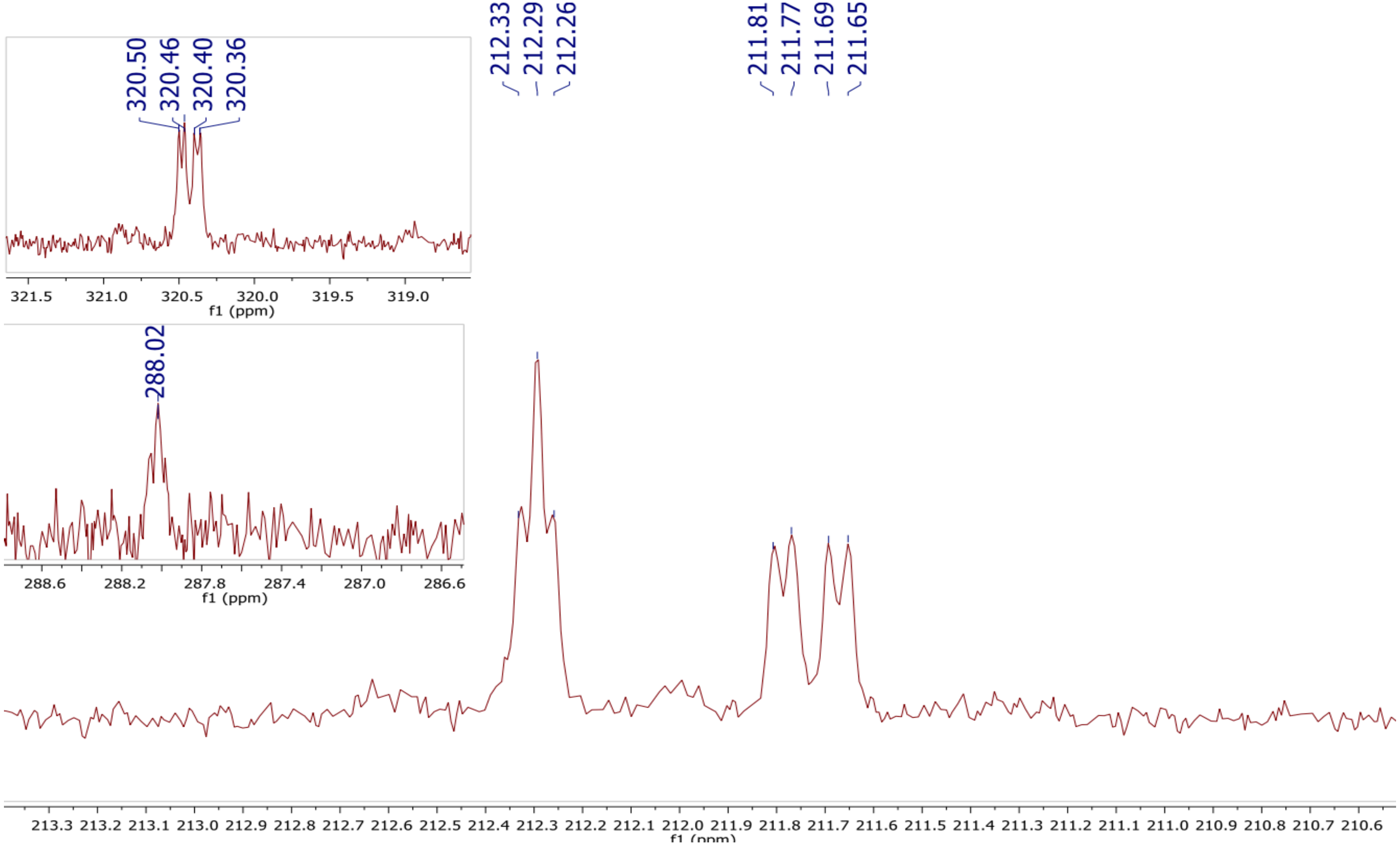
$^{31}P\{^{1}H\}$ NMR Data for Conversion of 3 to 4, 5 and 9 (*t* = 1 and 72 hours).

The apparent asymmetry in the tungsten satellites surrounding peak the peak at $\delta_P = 45.33$ ppm reflects the formation of the decomposition product WCl_4(dcpe), the resonance for which overlaps with the low frequency satellite. The peak at 54.7 ppm peak corresponds to **4**, while the AB system labelled ($CDCl_3$: $\delta_A = 45.33$; $\delta_B = 26.27$) is of **5**.



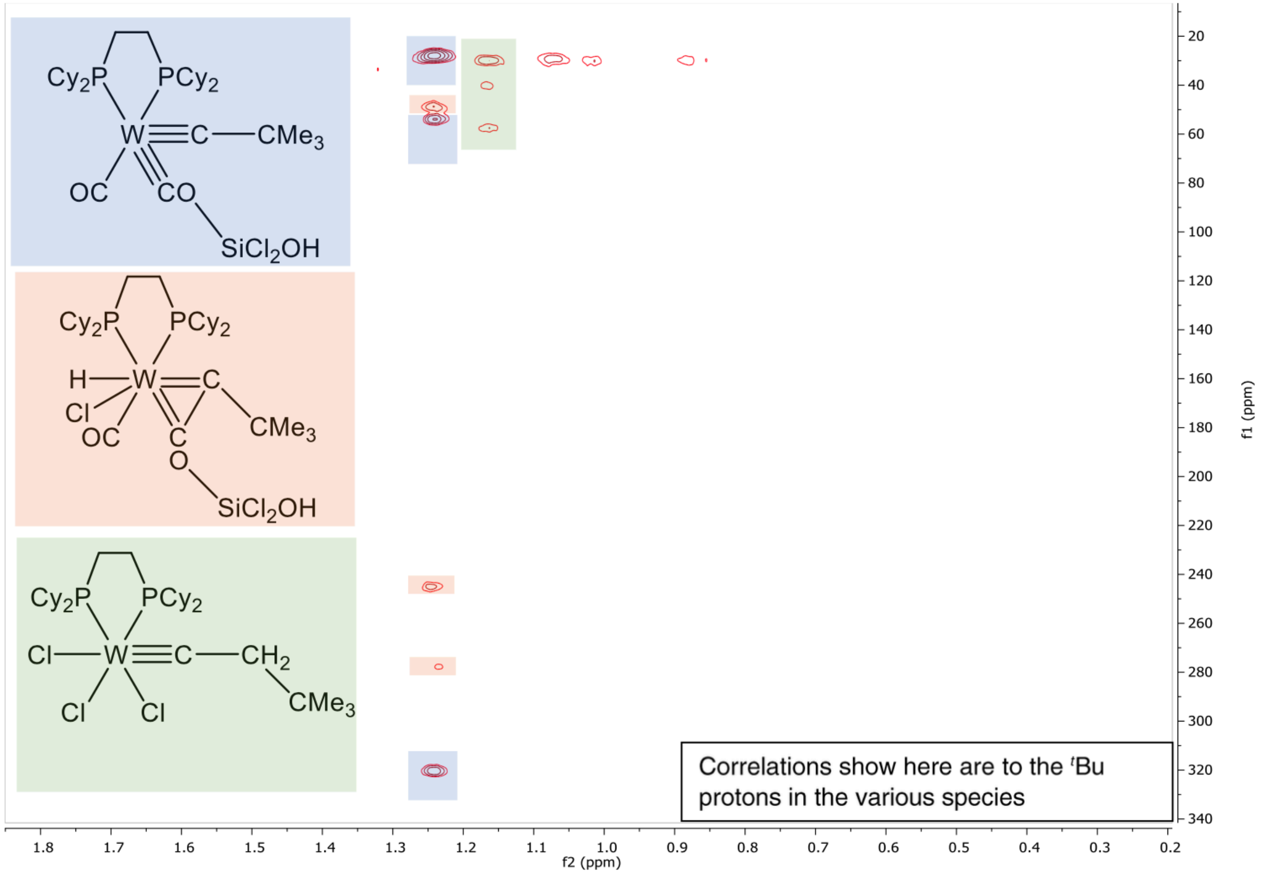
Low-Field $^{13}C\{^{1}H\}$ NMR Data for Conversion of 4 to 5 and 6.

The resonance at δ_C = 212.3 appears as an apparent triplet. The weak resonance at δ_C = 288.0 is attributed to the neohexylidyne complex **4**. The carbyne resonance for **5** appears as a doublet of doublets centred at δ_C = 230.4.



^{1}H-^{13}C HMBC (3-4 bond optimised).

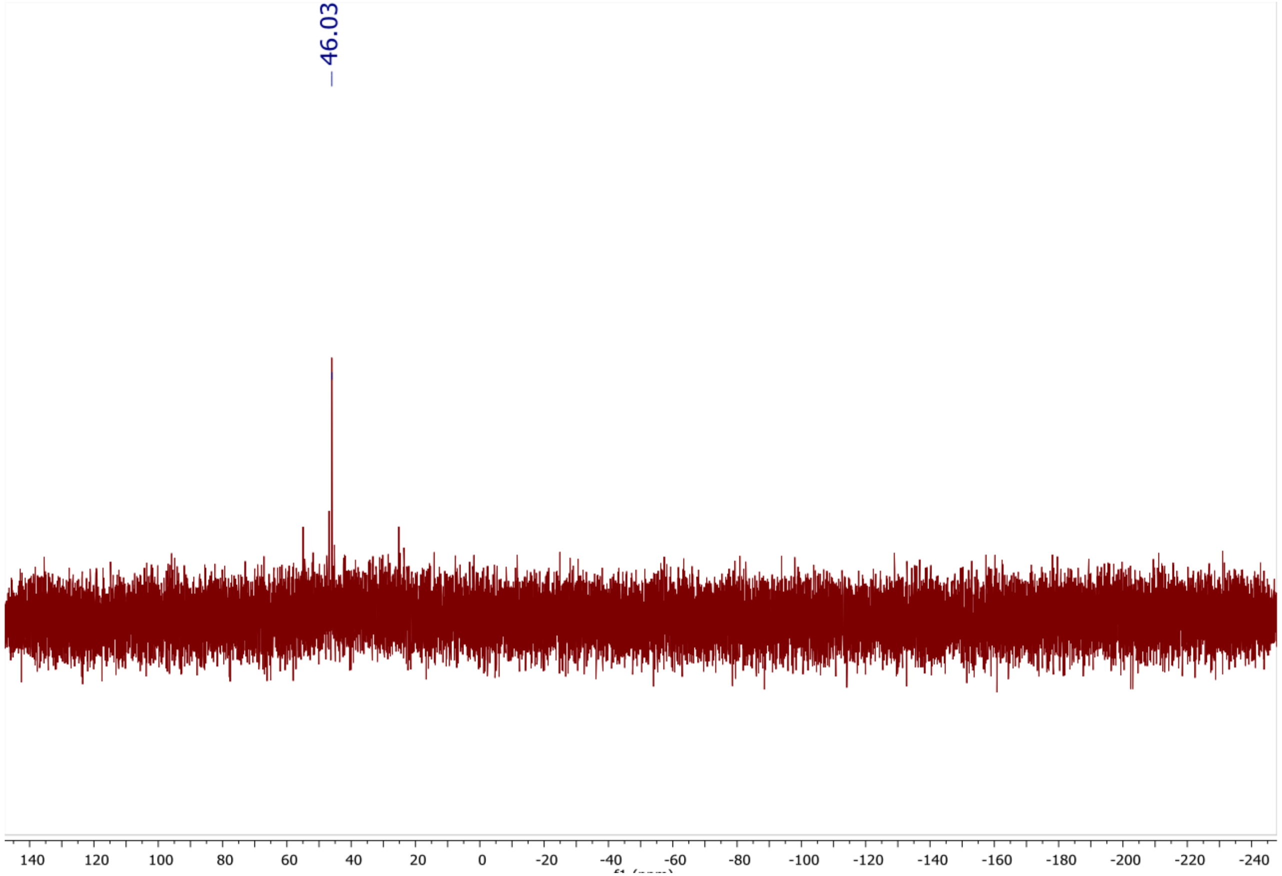
Correlations are colour coded t their respective species. Correlations between the methylene group are NMR silent due to the likely nature of H/D exchange with adventitious D_2O.



Correlations show here are to the ^{t}Bu protons in the various species

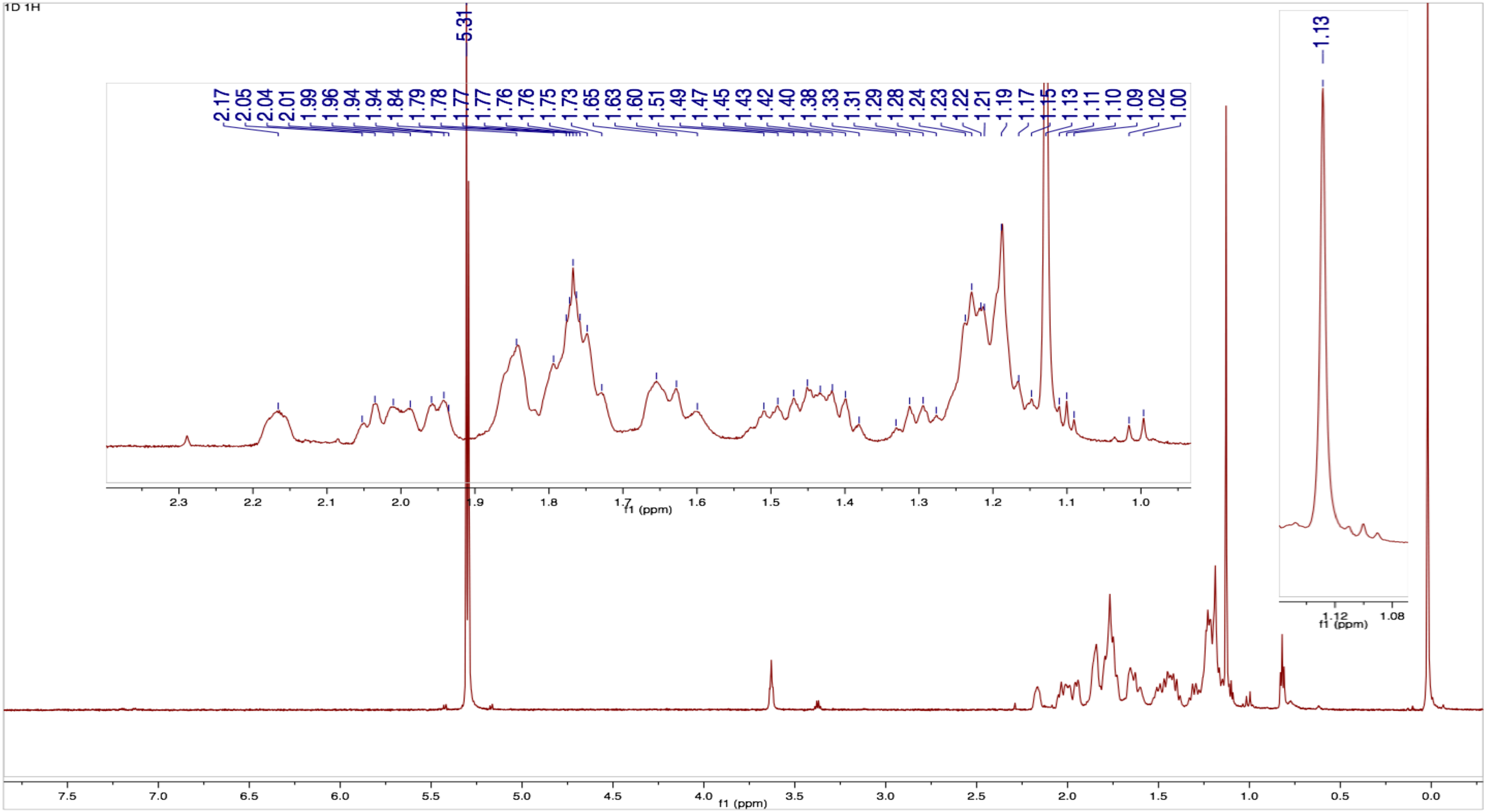
NMR Data for WCl_4(dcpe) (**9**) and neohexene in final product (t = 120 hrs at room temperature).

$^{31}P\{^1H\}$ NMR Spectrum

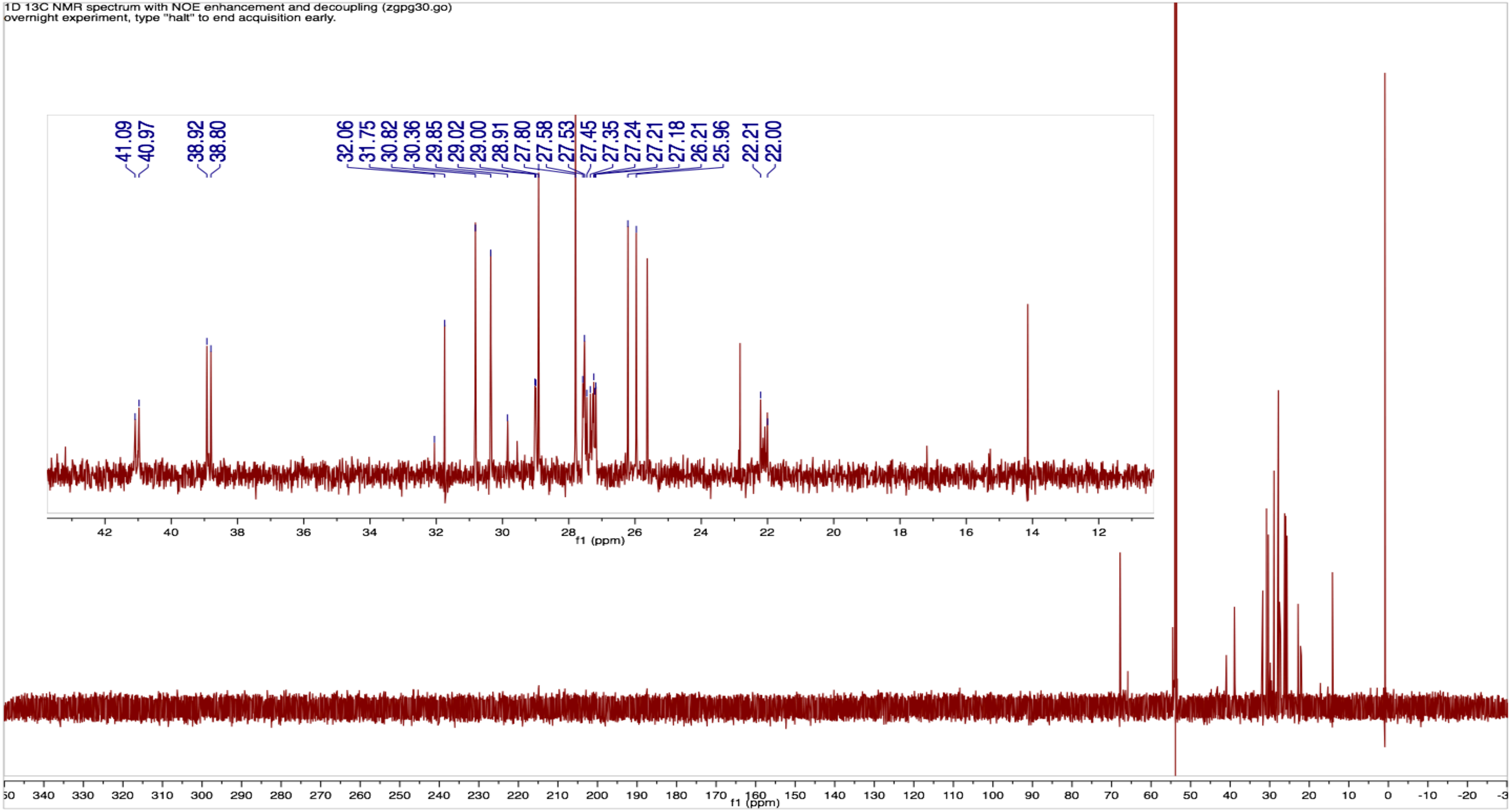


The dramatic reduction in signal to noise is consistent with the formation of NMR silent [W(=O)Cl_3(dcpe)] (**7**), with only trace amounts of (**6**) remaining in solution.

^{1}H NMR Spectrum of [W(≡C^{t}Bu)(SiCl$_3$)(CO)$_2$(dcpe)] **3**



$^{13}C\{^1H\}$ NMR Spectrum of $[W(\equiv C^tBu)(SiCl_3)(CO)_2(dcpe)]$ **3**



$^{31}P\{^1H\}$ NMR Spectrum of [W(≡C^tBu)($SiCl_3$)$(CO)_2$(dcpe)] **3**