

ESI for

Neutral and cationic tungsten(VI) fluoride complexes with neutral tertiary phosphine and arsine coordination

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Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1} . UV/visible spectra were recorded in a sealed PTFE cell with silica window on neat samples, using the diffuse reflectance attachment, in a Perkin Elmer 750S spectrometer. ^1H , $^{19}\text{F}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker AV 400 spectrometer and are referenced to the residual proton resonance from the solvent, external CFCl_3 and 85% H_3PO_4 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use by distillation over CaH_2 . WF_6 was obtained from Fluorochem. Ligands were obtained commercially (Sigma Aldrich or Strem) and used as received, except for $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ ¹ and $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ ² which were made as described. All reactions were carried out under dinitrogen in rigorously dry solvents, using Schlenk and glove box techniques. The isolated complexes decomposed slowly at ambient temperatures but could be stored in sealed tubes in a freezer (-18°C) for some weeks.

CARE: WF_6 is highly corrosive and causes serious burns on skin contact, while the complexes described below produce HF on hydrolysis. Appropriate safety equipment should be worn.

$[\text{WF}_6(\text{AsMe}_3)]$: A solution of AsMe_3 (0.12g, 1.0 mmol) in CH_2Cl_2 (10 mL) was frozen in liquid nitrogen and WF_6 (0.35g, 1.2 mmol) condensed in under vacuum. The mixture was allowed to warm to room temperature when it became deep orange-red. After 1 h the solvent was removed *in vacuo* leaving an orange-red powder that was stored in a sealed ampoule in a freezer. The solid turned deep blue on contact with moisture. Yield 0.40 g, 85%. Required for $\text{C}_3\text{H}_9\text{AsF}_6\text{W}$ (417.9), C, 8.62; H, 2.17. Found: C, 8.40; H, 2.15%. ^1H NMR (CD_2Cl_2 , 293 K): δ = 1.91 (s); (183 K): 1.92 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 293 K): δ = +130.7 (s); (183 K): +127.0 (s). IR (Nujol/ cm^{-1}): 620 (s, vbr) W-F. UV/vis (diffuse reflectance/ cm^{-1}): 22 700 (v br).

$[\text{WF}_6(\text{AsEt}_3)]$: A similar reaction using AsEt_3 produced an extremely moisture sensitive deep orange-red oil. This decomposed immediately in air turning dark blue and was significantly decomposed in

CD₂Cl₂ solution after 30 min. becoming pale yellow. The oil also lost colour overnight at room temperature precluding obtaining a microanalysis. The freshly prepared solution in CD₂Cl₂ had: ¹H NMR (CD₂Cl₂, 293 K): δ = 1.47 (m), 2.41 (m). ¹⁹F{¹H} NMR (CD₂Cl₂, 293 K): δ = +134.4 (s). IR (Nujol/cm⁻¹): 622 (s, vbr) W-F.

[WF₄{o-C₆H₄(AsMe₂)₂}]₂[WF₇]₂: A solution of o-C₆H₄(AsMe₂)₂ (0.29 g, 1 mmol) in anhydrous CH₂Cl₂ (15 mL) was frozen in liquid nitrogen and WF₆ (0.6 g, 2 mmol) was condensed in. The mixture was allowed to warm slowly to ambient temperature and assumed an intense orange-red colour on melting. The solution was stirred for 30 min., concentrated *in vacuo* to ~ 5 mL, and the orange-red solid that precipitated was filtered off and dried *in vacuo*. Yield 0.44 g, 60%. Required for C₂₀H₃₂As₄F₁₈W₃ (1465.6): C, 16.4; H, 2.2. Found: C, 16.9; H, 2.2%. ¹H NMR (CD₃CN, 293 K): δ = 2.42 ([24H], s, Me), 7.92 ([4H], m, o-C₆H₄), 8.03 ([4H], m, o-C₆H₄). ¹⁹F{¹H} NMR (CD₃CN, 293 K): δ = 142.8 (s), -25.9 (s, ¹J_{WF} = 88 Hz). IR (Nujol/cm⁻¹): 650 (sh), 615 (b,s), 575 (m), 554 (m), 332 (s) W-F. UV/vis (diffuse reflectance/cm⁻¹): 20 800 (v br), 31 500 (s).

[WF₄{o-C₆H₄(PMe₂)₂}]₂[WF₇]₂: A solution of o-C₆H₄(PMe₂)₂ (0.20 g, 1 mmol) in CH₂Cl₂ (15 mL) was frozen in liquid nitrogen and WF₆ (0.6 g, 2 mmol) was condensed in under vacuum. The mixture was allowed to warm to room temperature, when it became orange-yellow. After 30 min. the solvent was concentrated to ~ 5 mL *in vacuo*, precipitating a yellow-orange powder which was filtered off and dried *in vacuo*. Yield 0.24 g, 40%. Required for C₂₀H₃₂F₁₈P₄W₃ (1289.9), C, 18.6; H, 2.5. Found: C, 18.7; H, 2.6 %. ¹H NMR (CD₃CN, 293 K): δ = 2.26 (br s, [24H], Me), 7.80 (m, [4H], o-C₆H₄), 7.93 (m, [4H], o-C₆H₄). ¹⁹F{¹H} NMR (CD₃CN, 293 K): δ = 142.8 (s), -17.5 (quintet, ²J_{PF} = 67 Hz). ³¹P{¹H} NMR (CD₃CN, 293 K): δ = +122.3 (quintet, ²J_{PF} = 67 Hz); (CD₂Cl₂, 293 K): δ = +127.8 (quintet, ²J_{PF} = 67 Hz). IR (Nujol/cm⁻¹): 649 (sh), 612 (s, vbr), 578 (sh) 336 (m, br) W-F. UV/vis (diffuse reflectance/cm⁻¹): 23 100 (v br), 31 650 (s).

WF₆ / RS(CH₂)₂SR (R = Me, ⁱPr): A 1 : 2 mixture of the dithioether and WF₆ in rigorously anhydrous CH₂Cl₂, produced a yellow-brown solution upon melting. This became colourless on further warming (~ 210 K) and, on removing the volatiles *in vacuo*, both CH₂Cl₂ and WF₆ were removed, leaving a clear oil which proved to be the clean dithioether (¹H NMR evidence). The ¹⁹F{¹H} NMR spectrum showed only traces of F⁻. This indicates that adduct formation occurred at low temperatures, but that the adducts decomposed on warming. In the presence of trace water, after work up the oils contained a few white particles and the ¹⁹F{¹H} NMR spectrum showed [WOF₅]⁻ and [W₂O₂F₉]⁻. It is probable that the product here was mainly the unchanged dithioether, with trace amounts of sulfonium salts (*cf.* the NbF₅ thioether systems).³

X-ray experimental

Very small crystals from the $[\text{WF}_4\{o\text{-C}_6\text{H}_4(\text{EMe}_2)_2\}_2][\text{WF}_7]_2$ complexes were grown by evaporation of MeCN solutions in the glove box. Details of the crystallographic data collection and refinement parameters are given in Table 1. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ($\lambda = 0.71073 \text{ \AA}$) rotating ^1H NMR anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinements were performed with either SHELX(S/L)97 or SHELX(S/L)2013.⁴ H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. For the diarsine structure the F atoms in the $[\text{WF}_8]^{2-}$ dianion were disordered. Therefore, all of the F atoms were constrained to have the same displacement parameters. Given the disorder, it is not possible to exclude completely the possibility that the anion might be $[\text{WOF}_6]^{2-}$. The crystallographic data in cif format have been deposited as CCDC 1854218-1854219.

- 1 E. P. Kyba, S. T. Liu and R. L. Harris, *Organometallics*, 1983, **2**, 1877.
- 2 R. D. Feltham, A. Kasenally and R. S. Nyholm, *J. Organometal Chem.*, 1967, **7**, 285.
- 3 M. Jura, W. Levason, G. Reid and M. Webster, *Dalton Trans.*, 2009, 7610.
- 4 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.

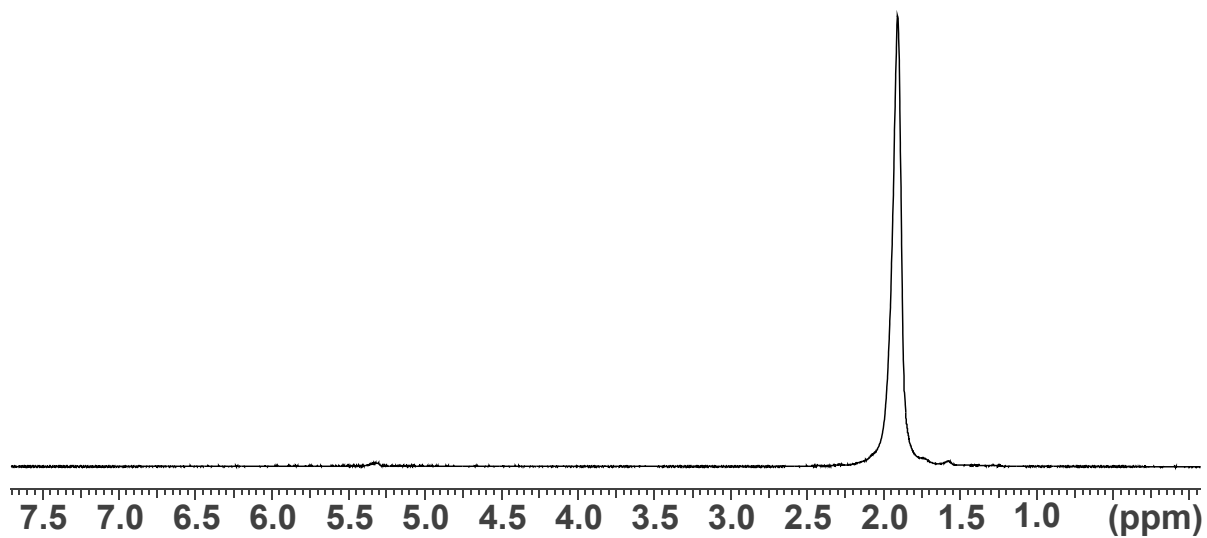
Table S1 X-ray crystallographic data^a

Compound	[WF ₄ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }] ₂ [WOF ₅] ₂ ·MeCN	[WF ₄ { <i>o</i> -C ₆ H ₄ (AsMe ₂) ₂ }] ₂ [WF ₈]
Formula	C ₁₁ H _{17.50} F ₇ N _{0.50} OP ₂ W _{1.50}	C ₂₀ H ₃₂ As ₄ F ₁₂ W ₂
<i>M</i>	643.47	1167.84
Crystal system	Orthorhombic	Orthorhombic
Space group (no.)	Pbca (61)	Fddd (70)
<i>a</i> /Å	16.7303(10)	13.1003(10)
<i>b</i> /Å	17.878(2)	21.3132(10)
<i>c</i> /Å	24.095(2)	21.3804(10)
α /°	90	90
β /°	90	90
γ /°	90	90
<i>U</i> /Å ³	7206.9(11)	5969.6(6)
<i>Z</i>	16	8
μ(Mo-K _α) /mm ⁻¹	9.826	12.188
<i>F</i> (000)	4784	4320
Total number reflns	39879	5922
<i>R</i> _{int}	0.052	0.037
Unique reflns	7082	1279
No. of params, restraints	424, 2	87, 1
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.041, 0.086	0.038, 0.104
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.068, 0.101	0.054, 0.112

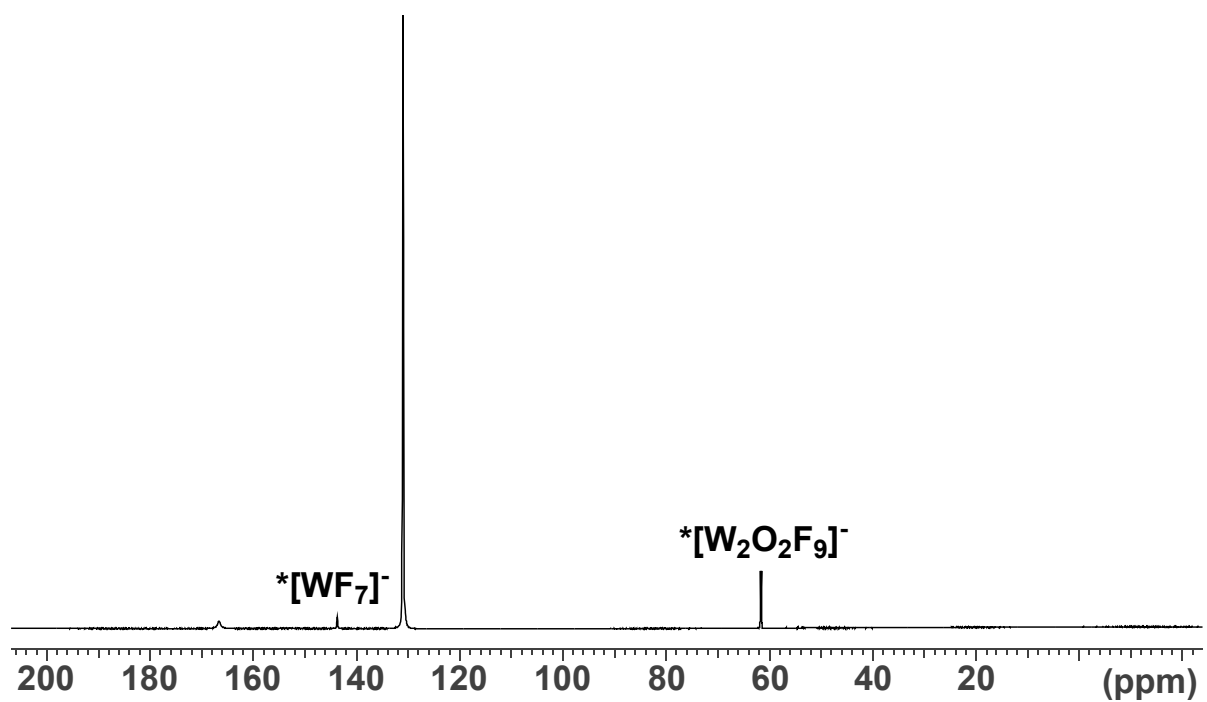
^a Common items: wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°. ^b $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}}$



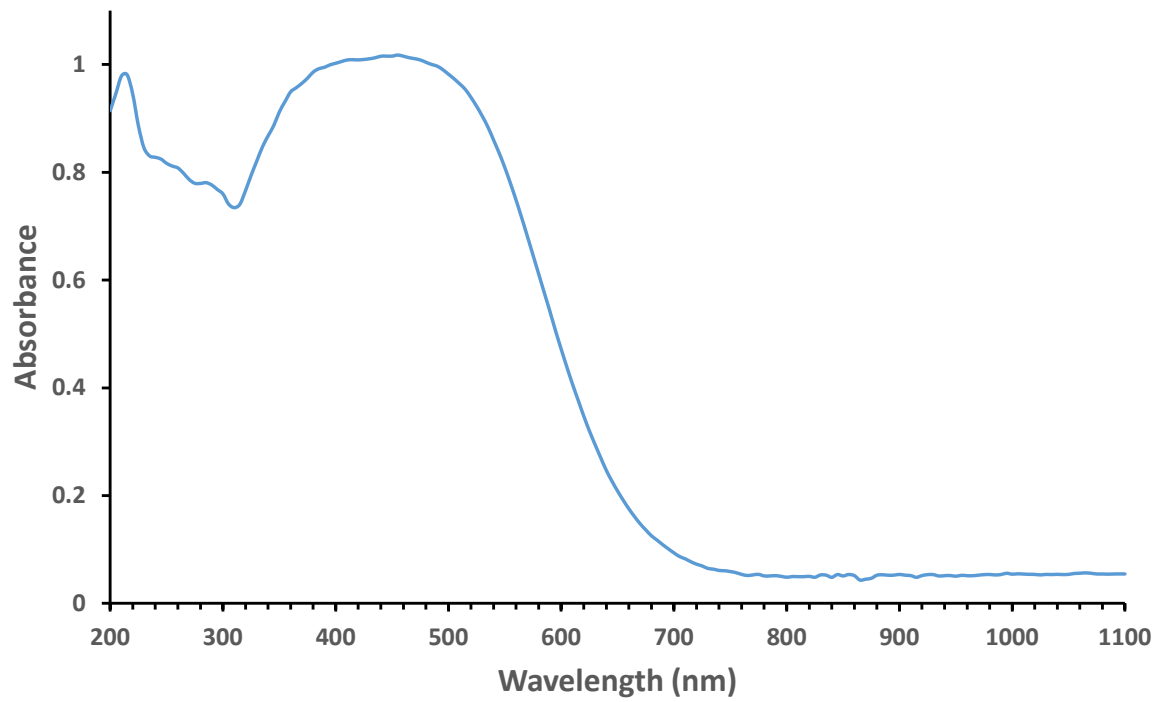
¹H NMR spectrum (400 MHz, CD₂Cl₂, 293 K):



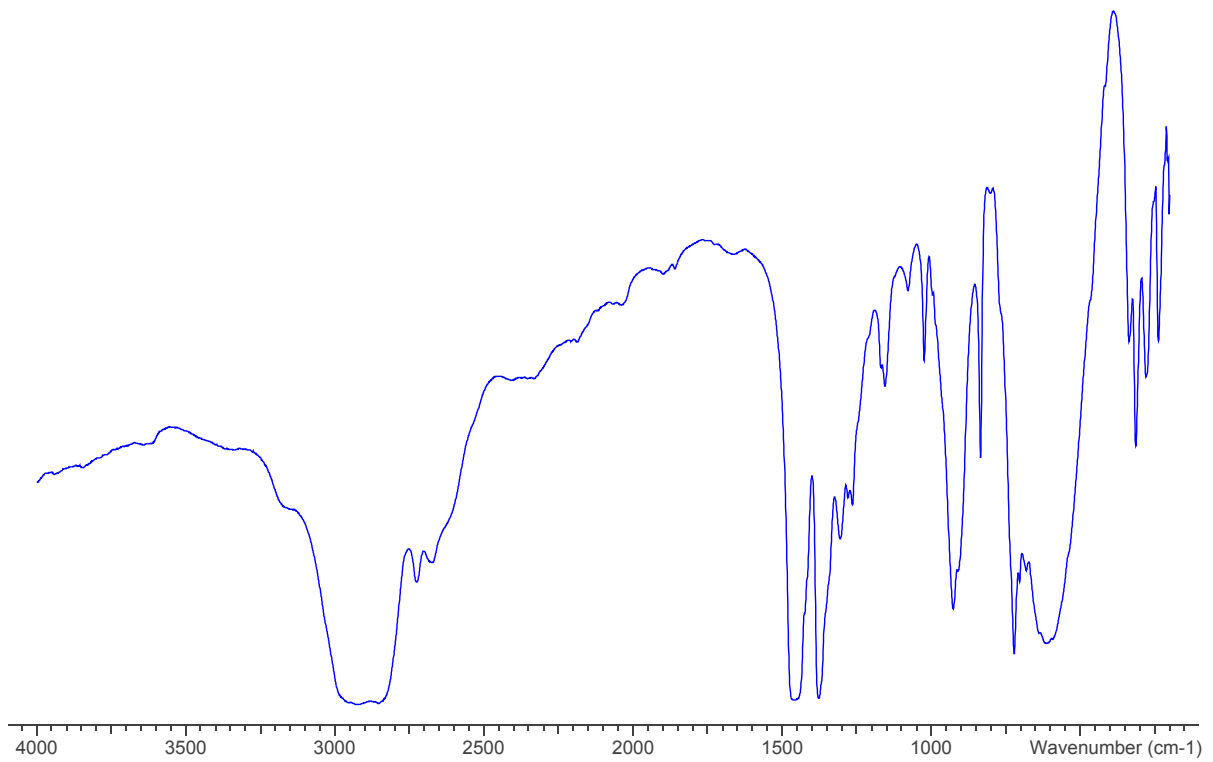
¹⁹F {¹H} NMR spectrum (CD₂Cl₂, 293 K):



UV-vis spectrum (diffuse reflectance):

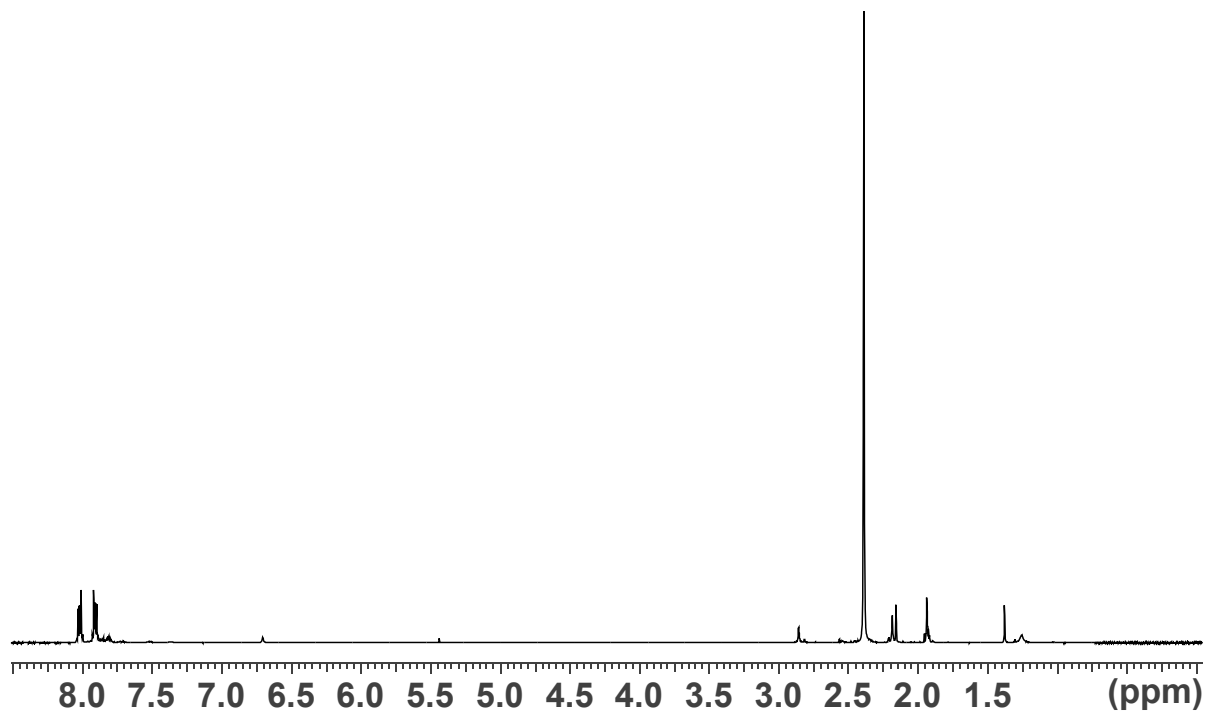


IR spectrum (Nujol):

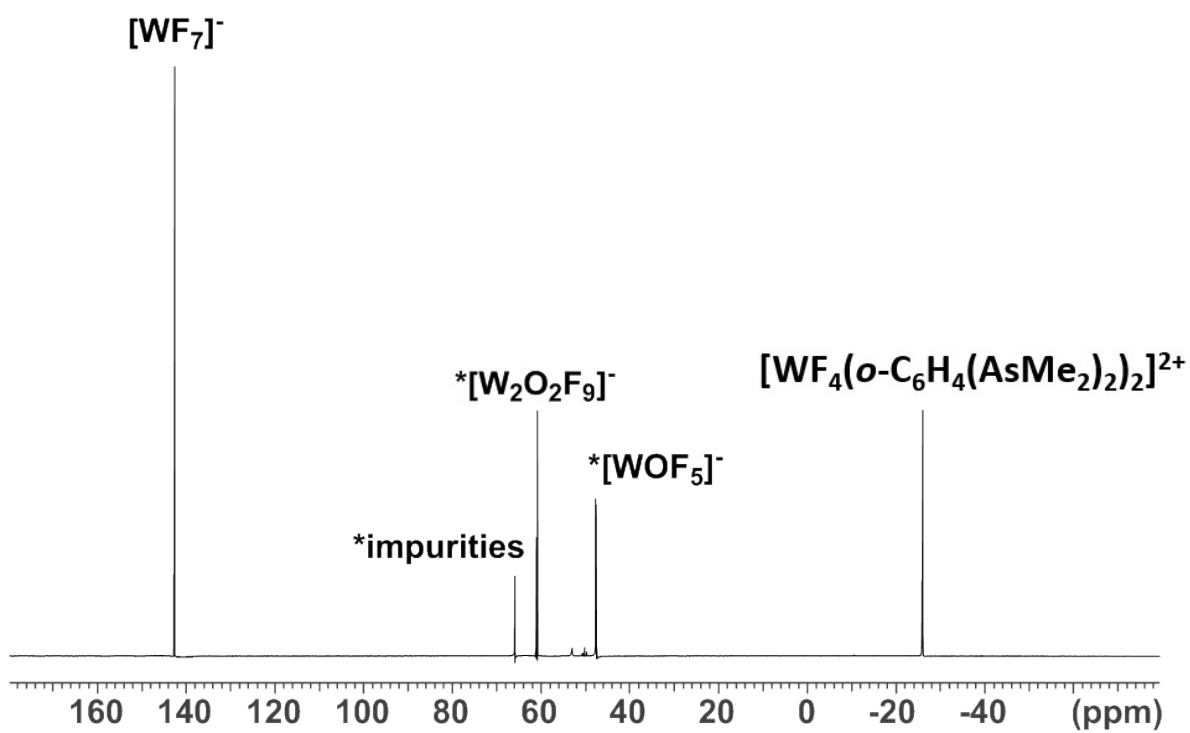




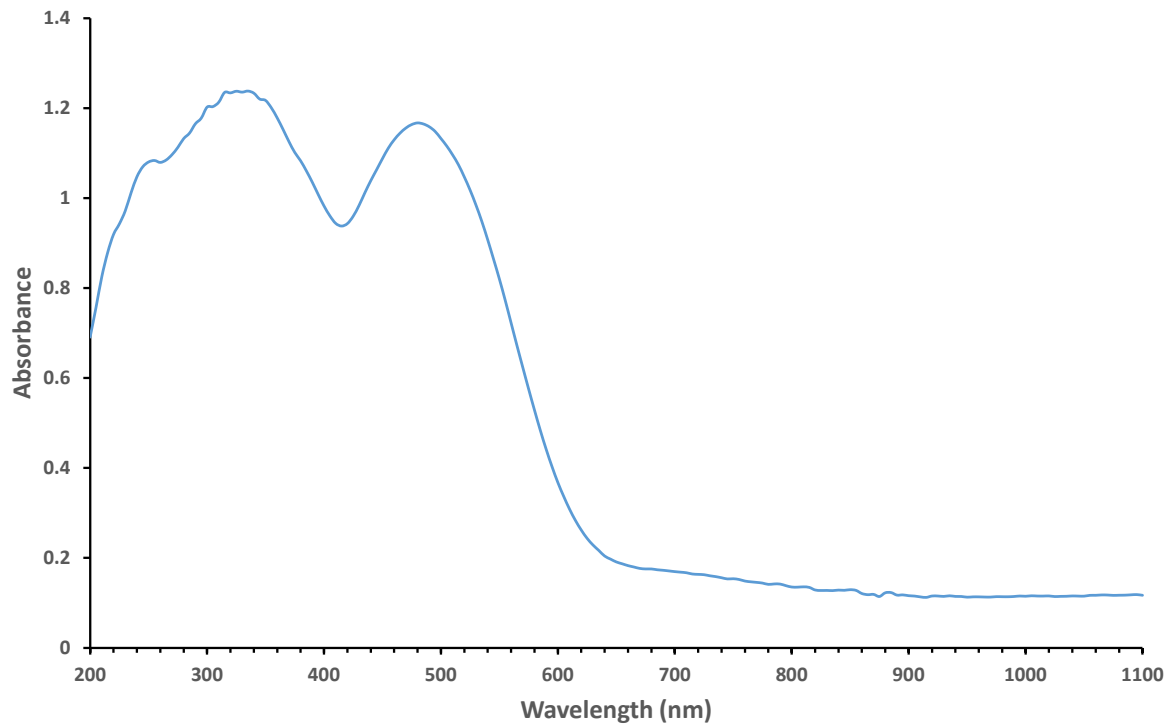
^1H NMR spectrum (400 MHz, CD_3CN , 293 K):



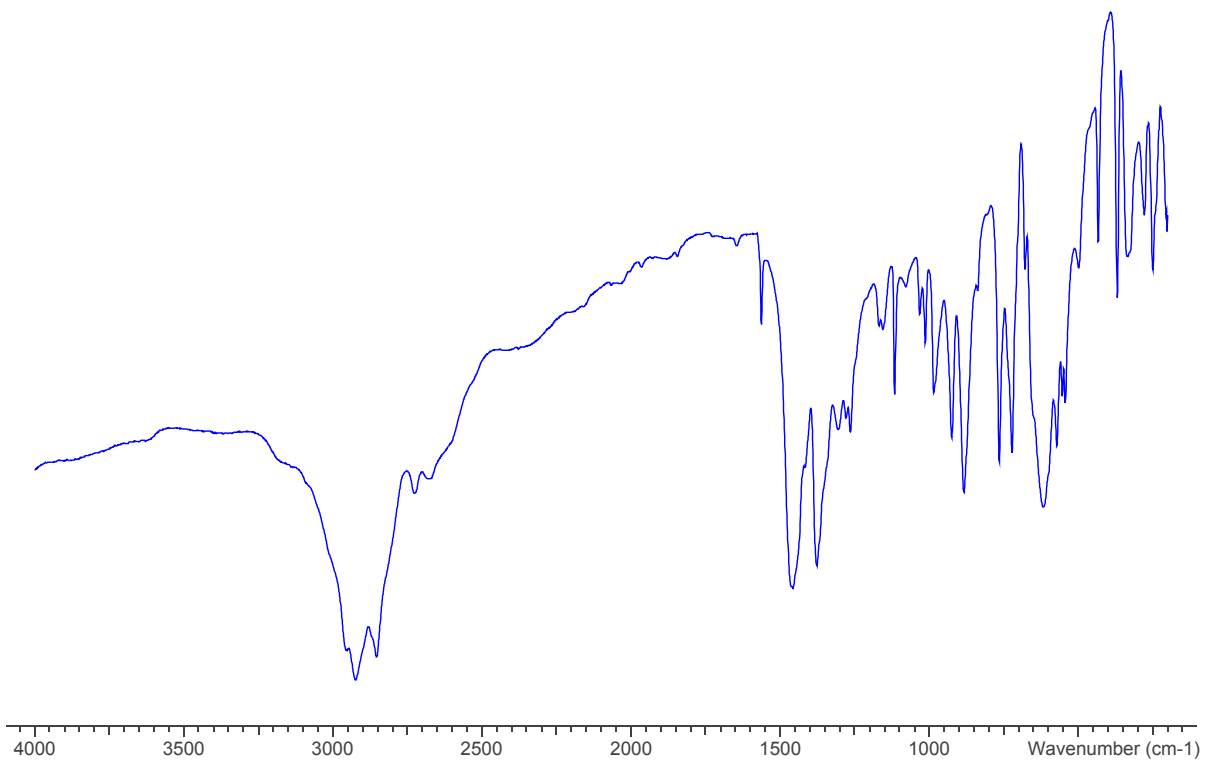
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3CN , 293 K):



UV-vis spectrum (diffuse reflectance):

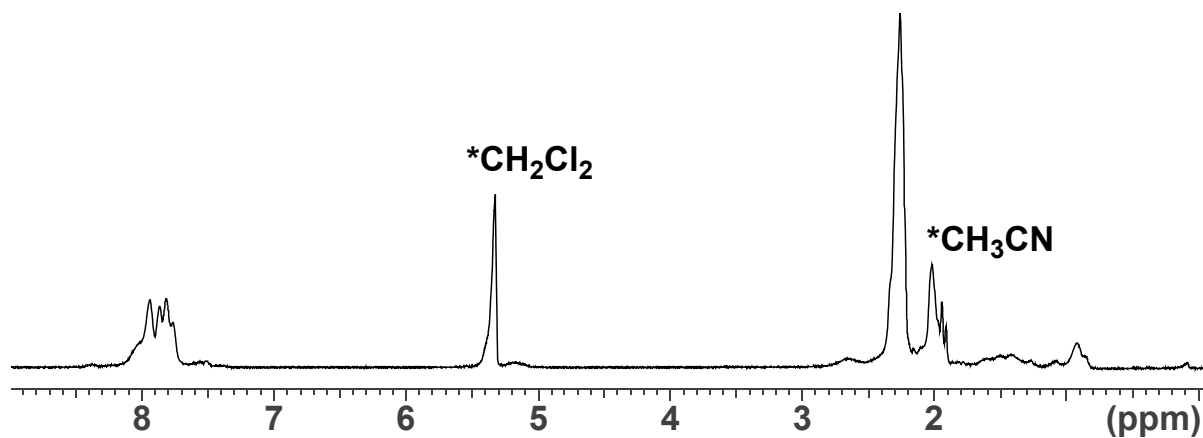


IR spectrum (Nujol):

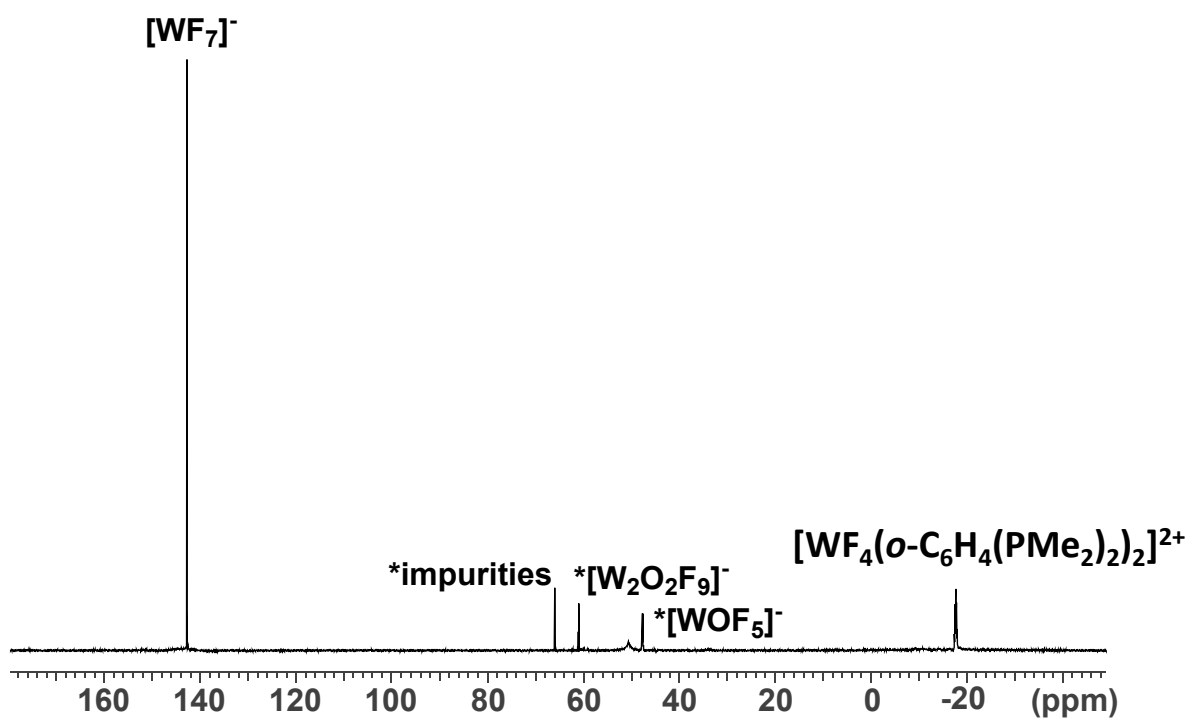




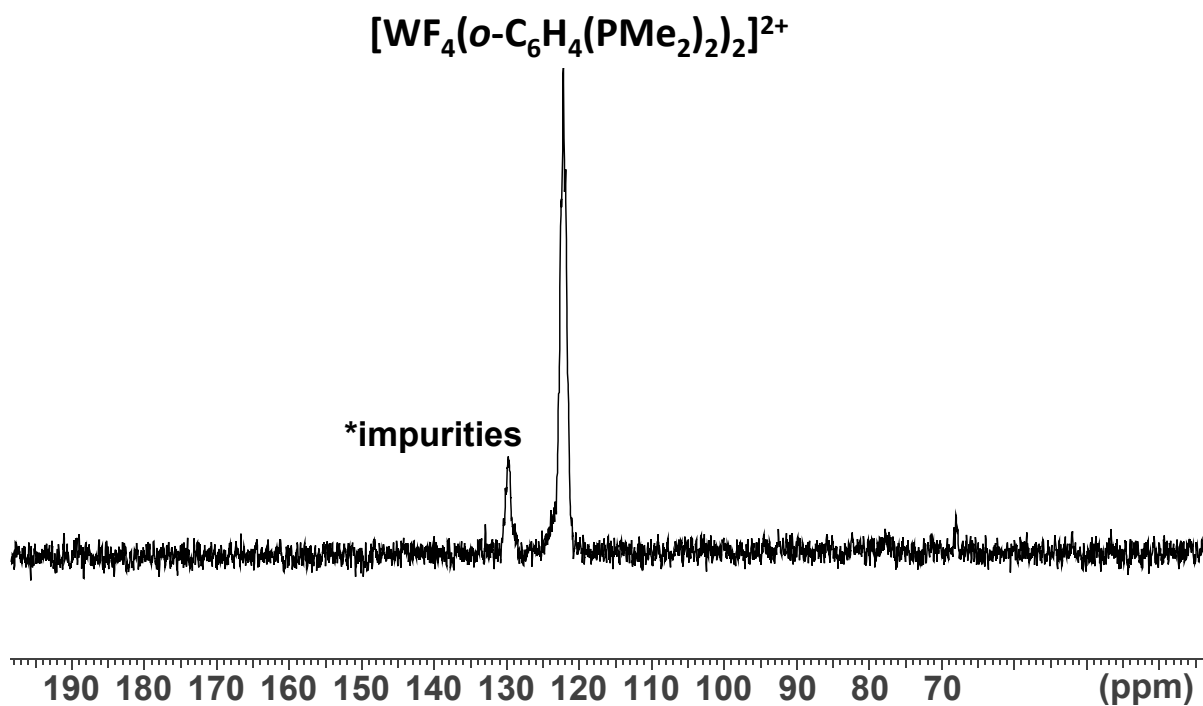
^1H NMR spectrum (400 MHz, CD_3CN , 293 K):



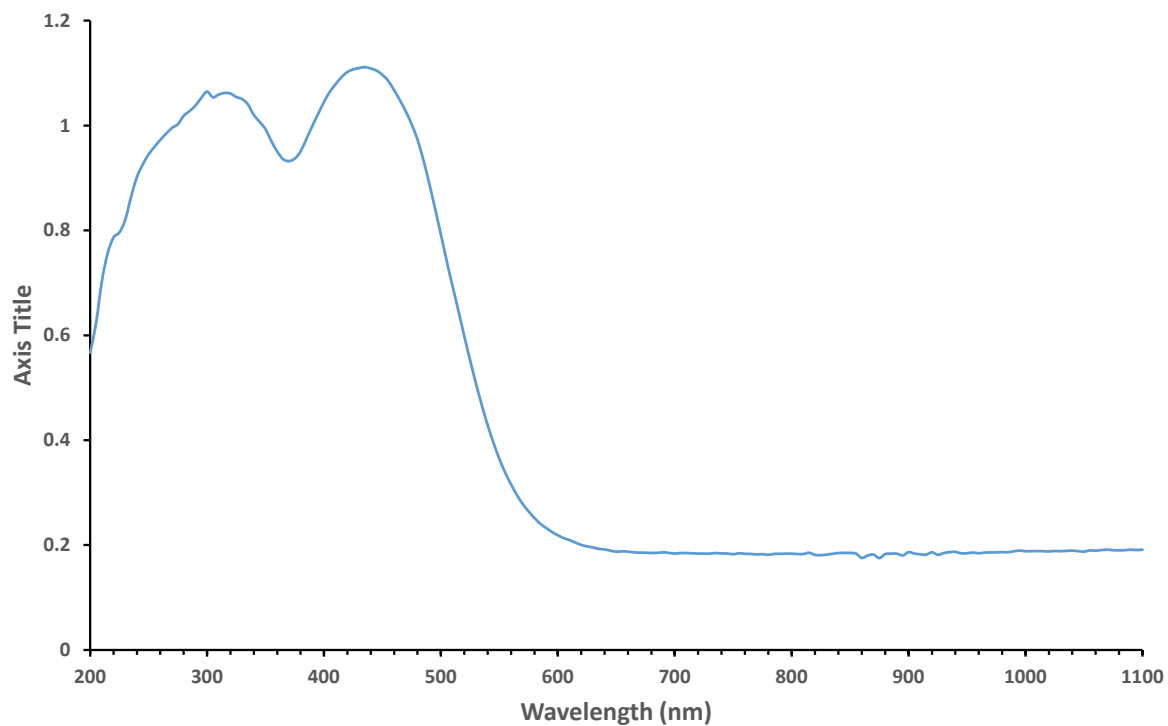
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3CN , 293 K):



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_3CN , 293 K):



UV-vis spectrum (diffuse reflectance):



IR spectrum (Nujol):

