Catonic Abnormal *N*-heterocyclic Carbene Ruthenium Complexes as Suitable Precursors for the Synthesis of Heterobimetallic Compounds

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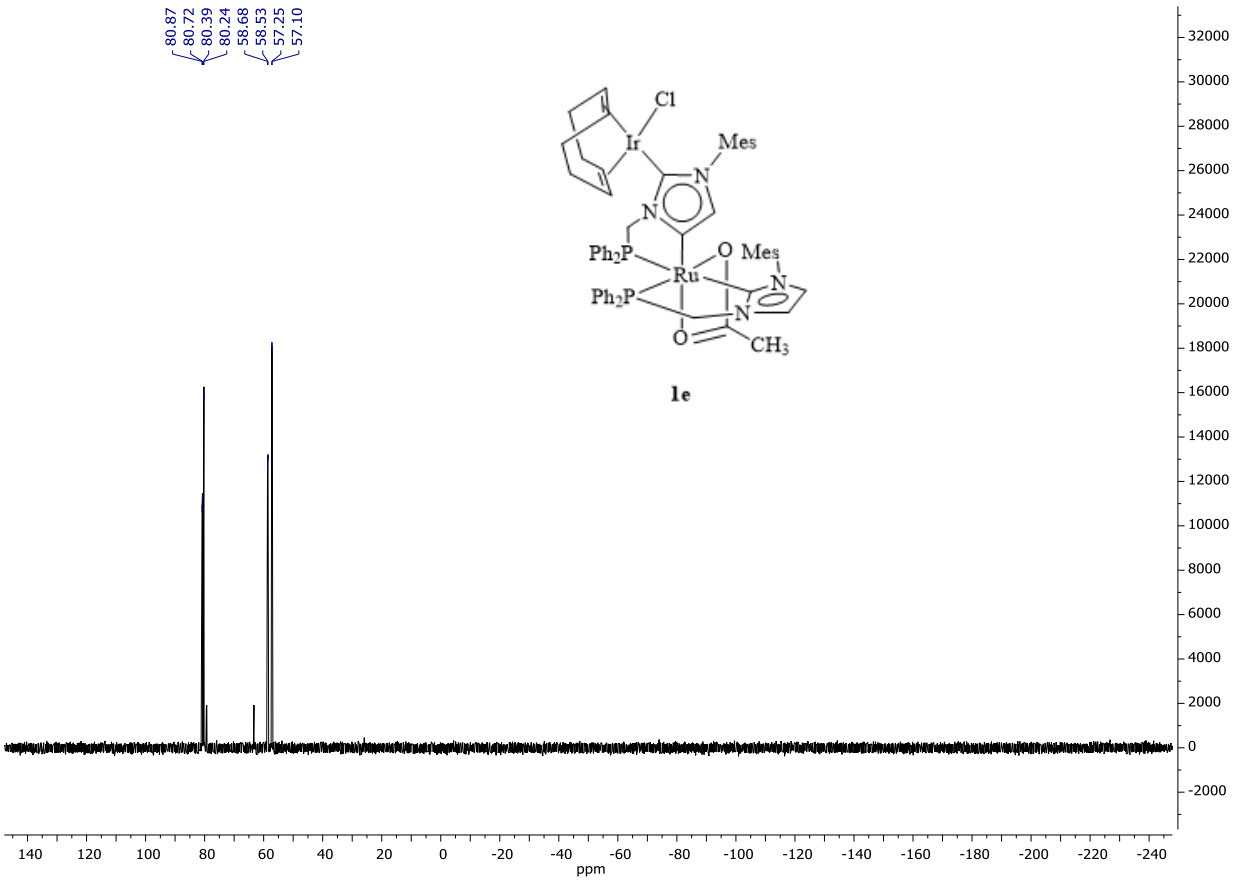

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of Complex **1e** in CD_2Cl_2 at 20 °C.

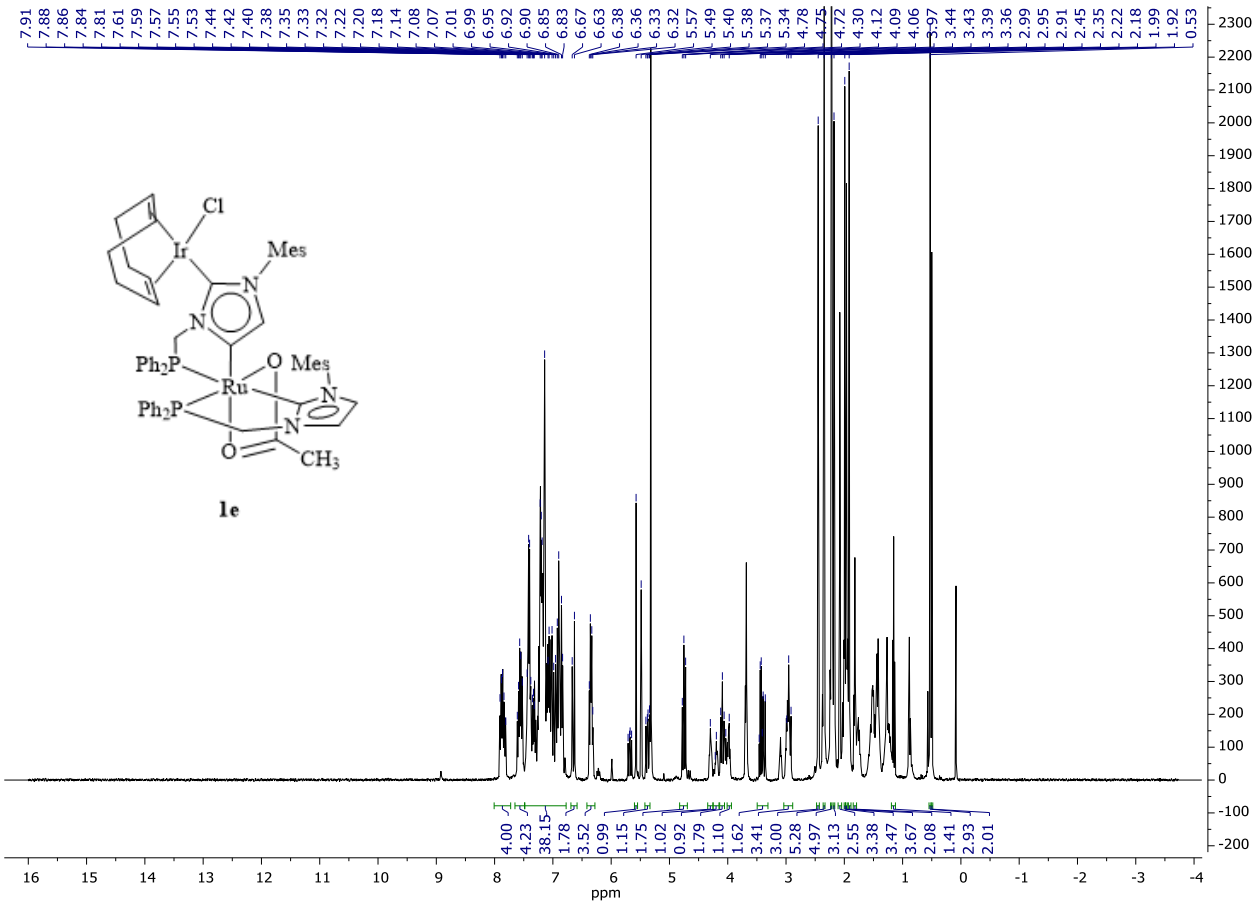

Figure S2. ^{1}H NMR spectrum (400.0 MHz) of Complex **1e** in CD_2Cl_2 at 20 °C.

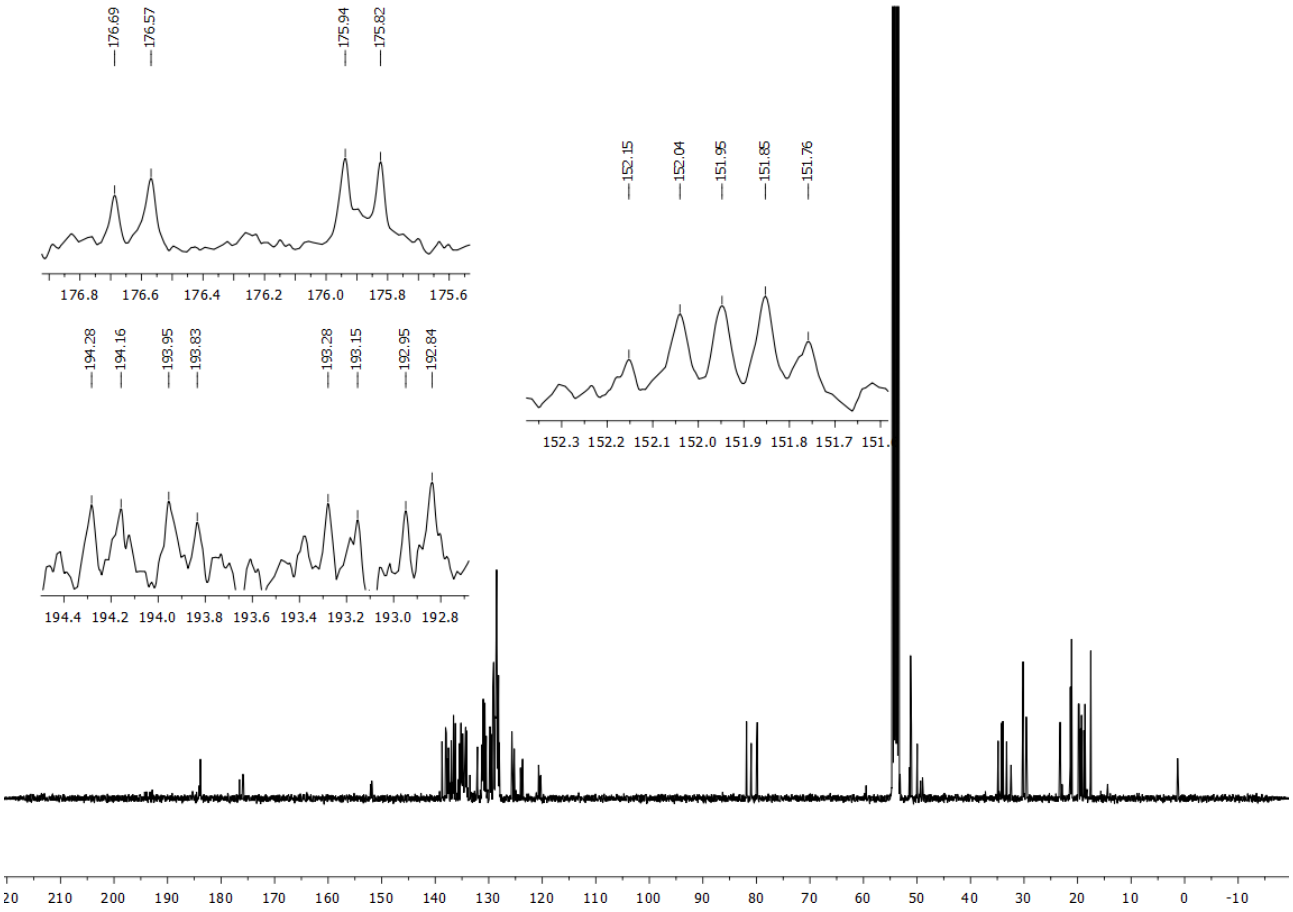

Figure S3. ^{13}C NMR spectrum (101.0 MHz) of Complex **1e** in CD_2Cl_2 at 20 °C with highlighted carbene signals.

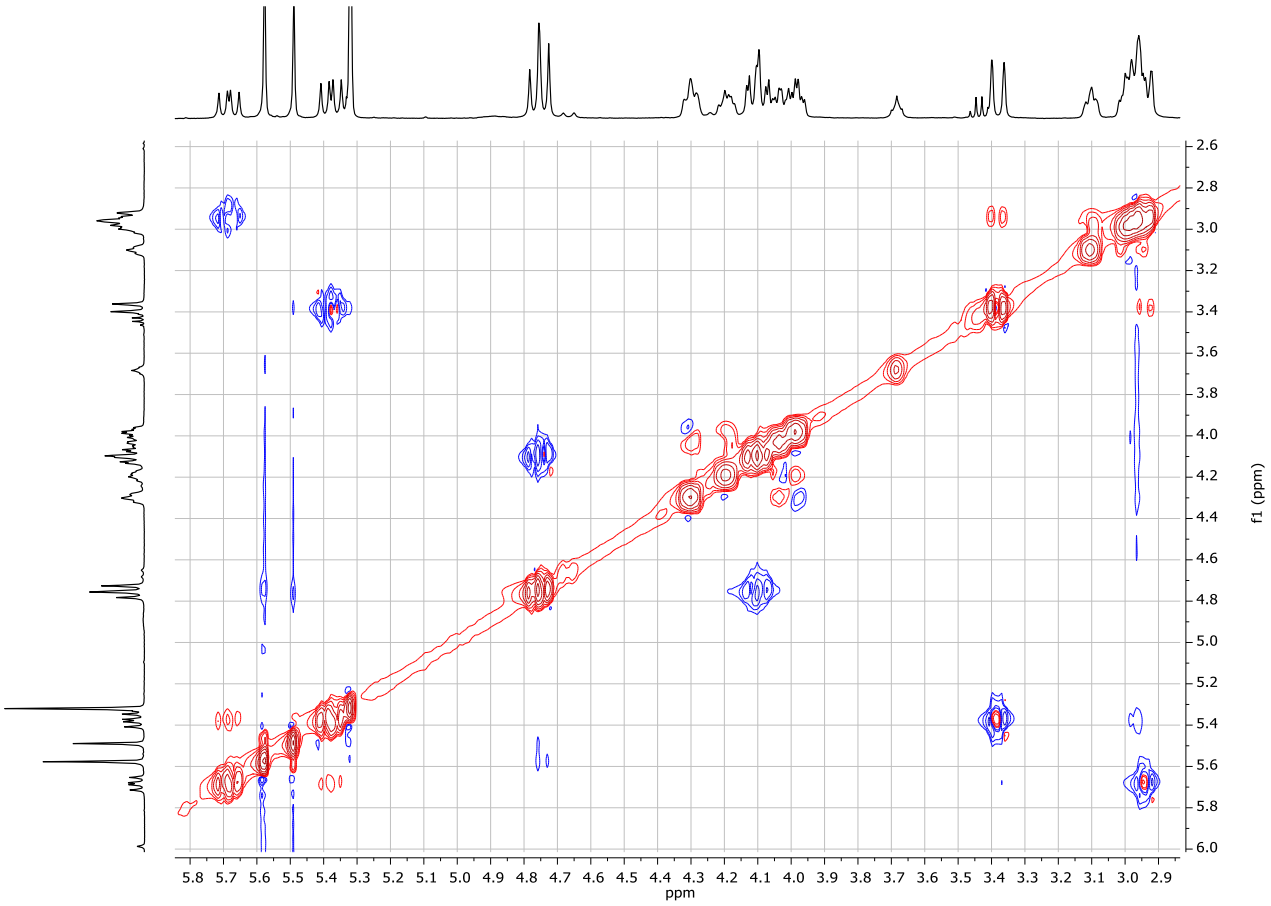

Figure S4. NOESY NMR spectrum (400.13 MHz) of complex **1e** in CD_2Cl_2 at 20 °C.

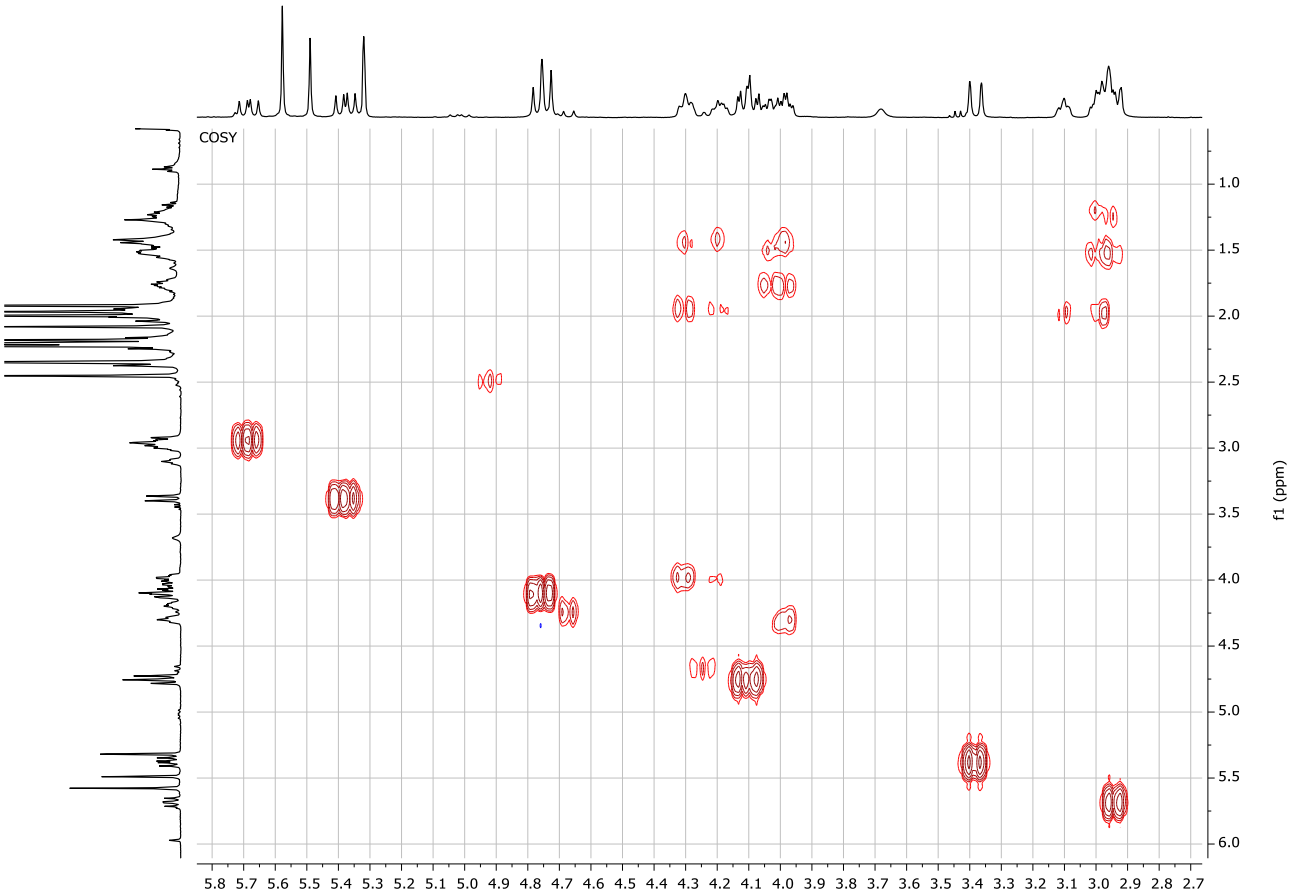

Figure S5. COSY NMR spectrum (400.13 MHz) of **1e** in CD_2Cl_2 at 20 °C.

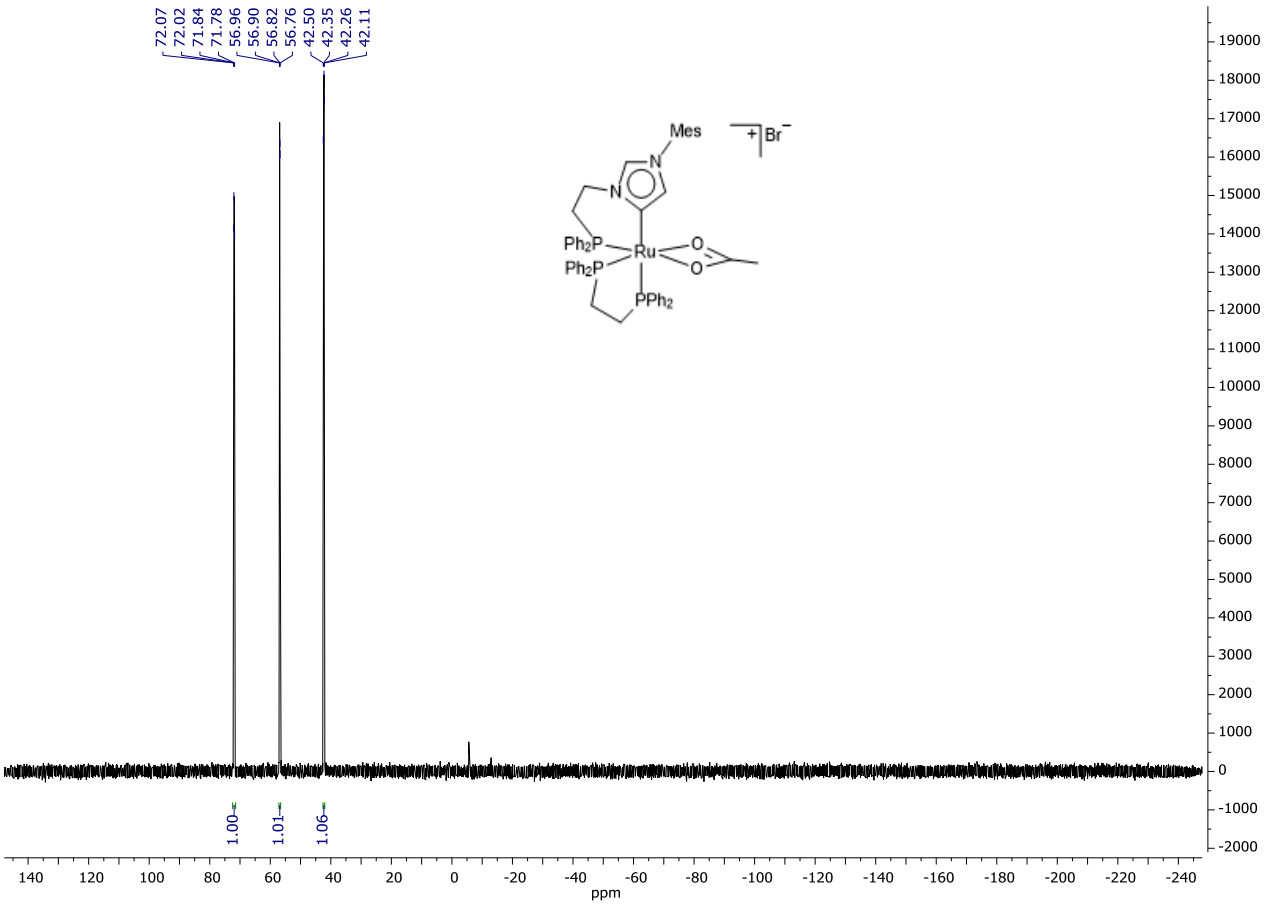

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of Complex **2b** in CD_2Cl_2 at 20 °C.

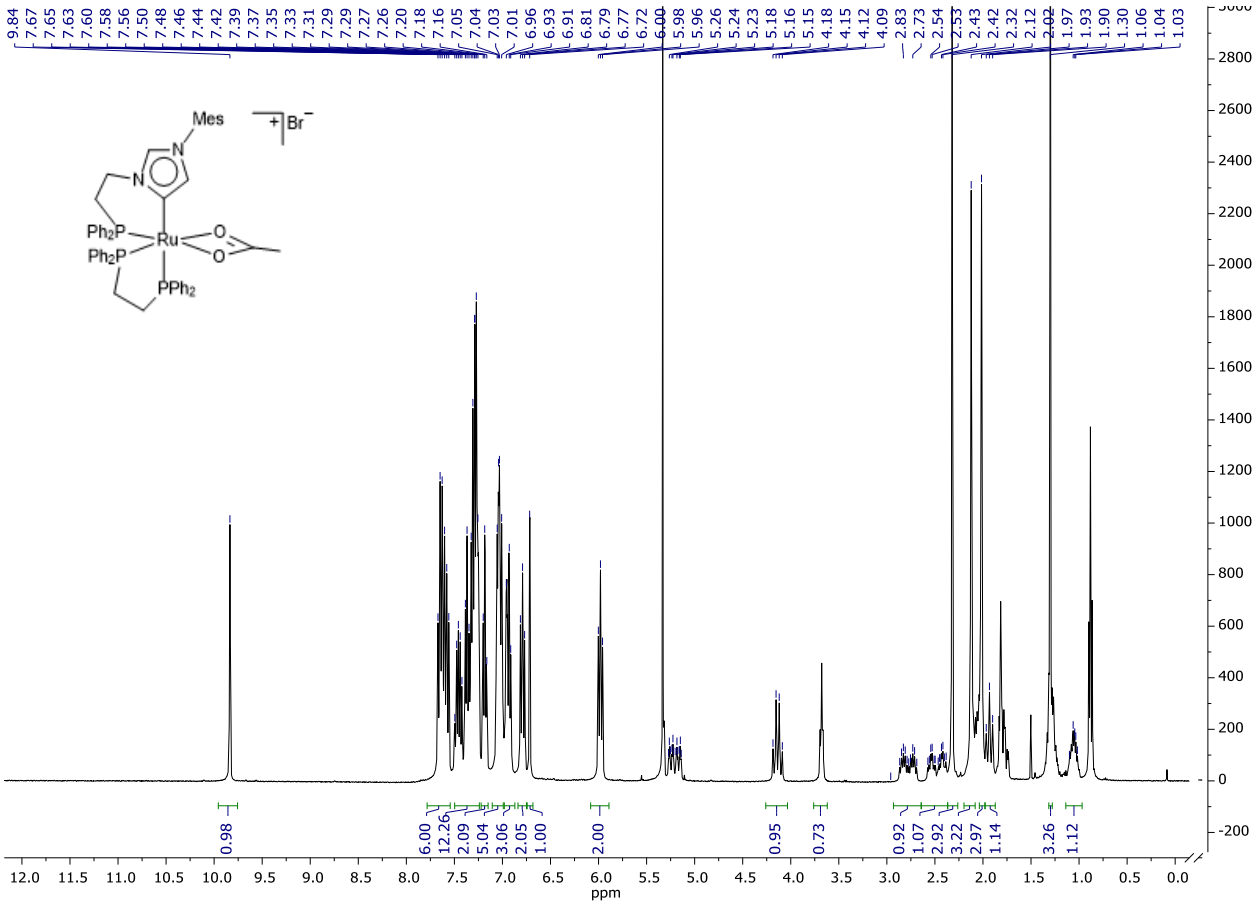

Figure S7. ^{1}H NMR spectrum (400.0 MHz) of Complex **2b** in CD_2Cl_2 at 20 °C.

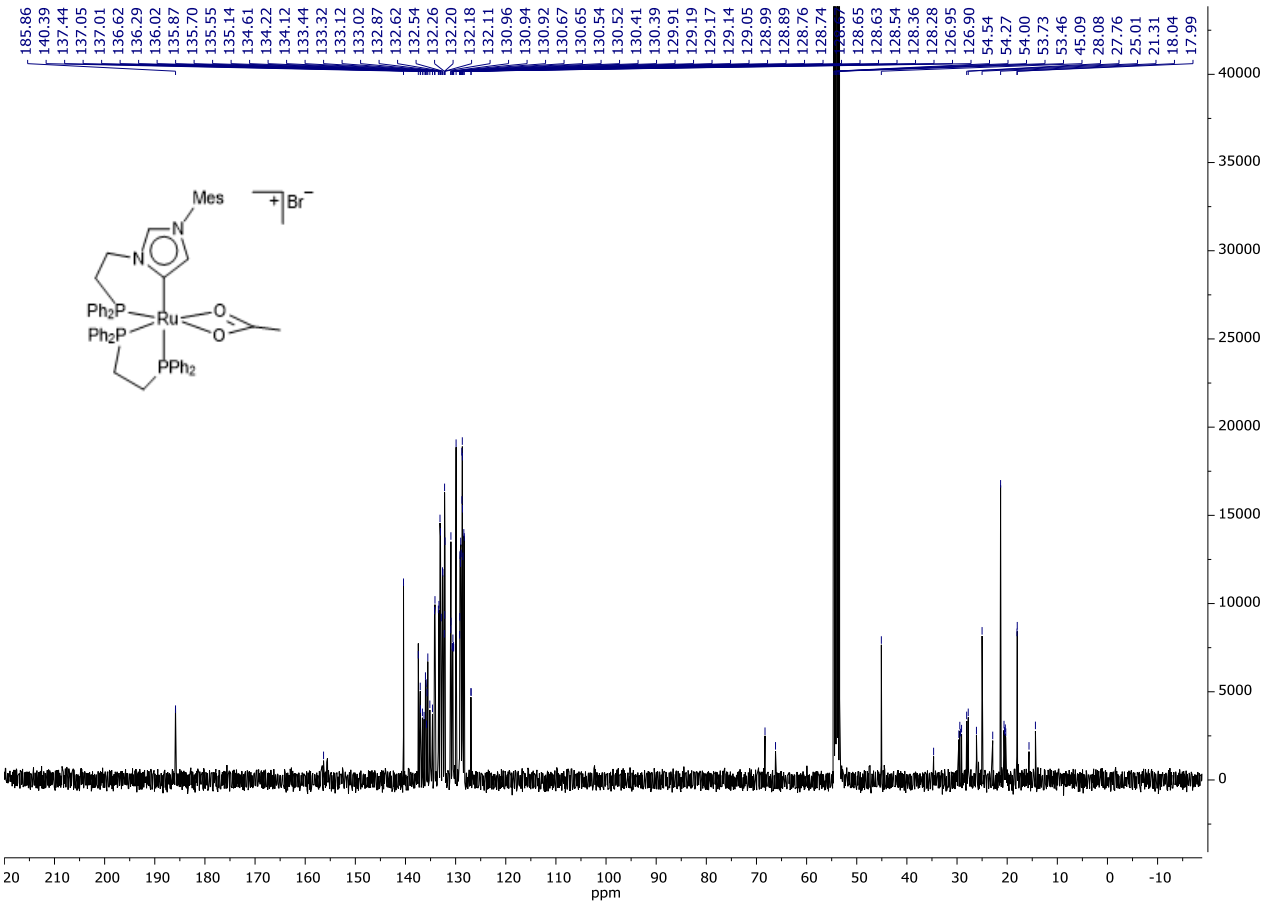

Figure S8. ^{13}C NMR spectrum (101.0 MHz) of Complex **2b** in CD_2Cl_2 at 20 °C.

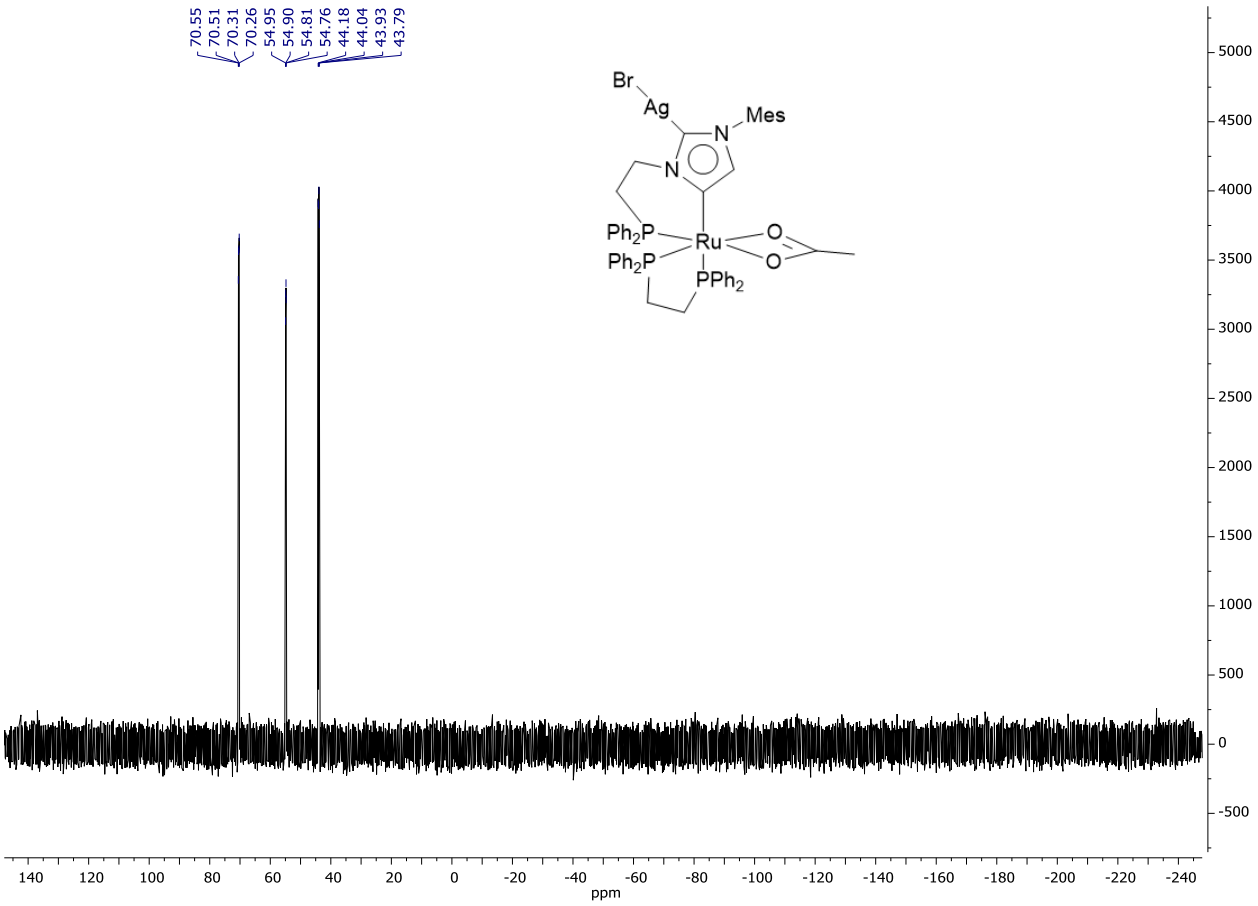

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of Complex **2c** in THF-*d8* at 20 °C.

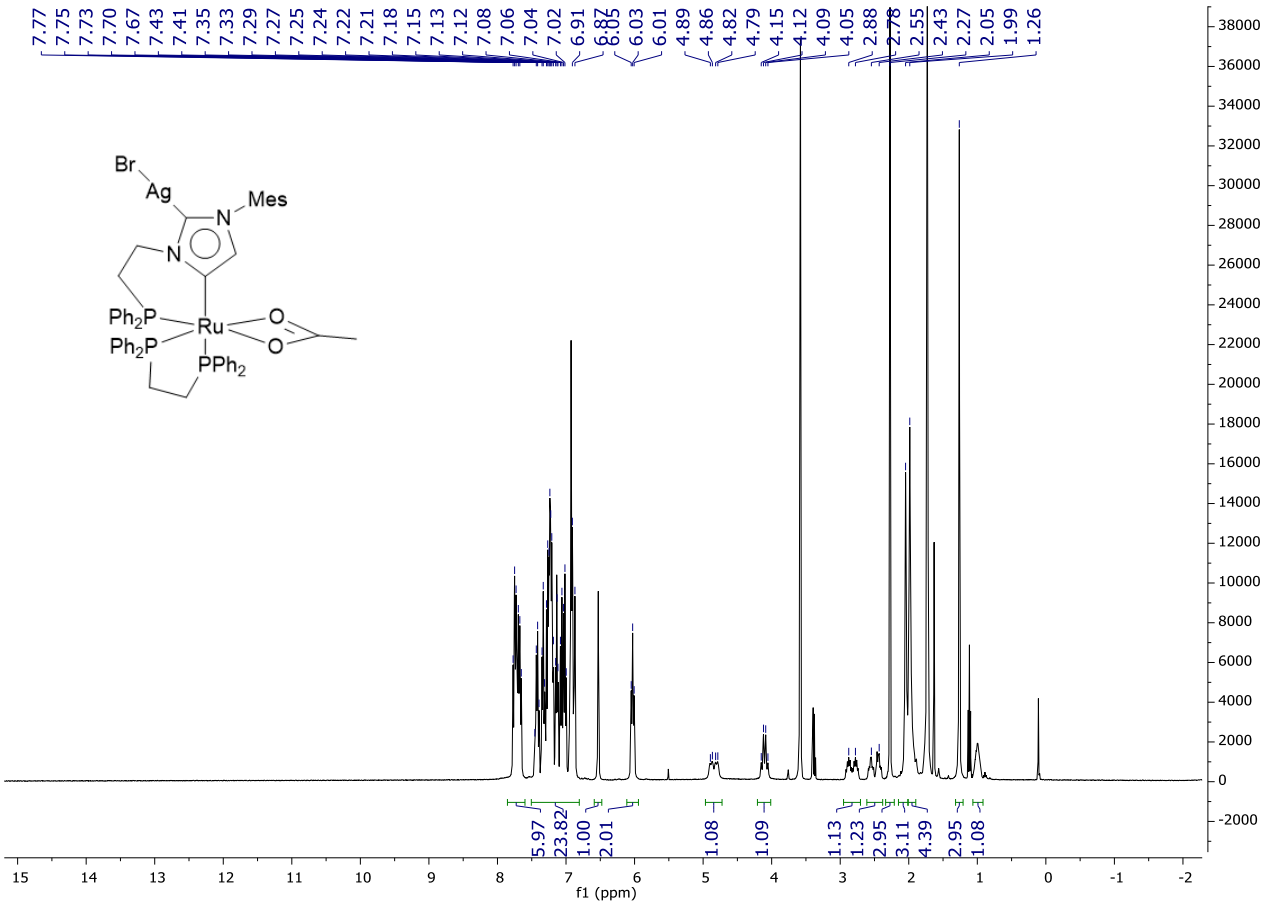

Figure S10. ^{1}H NMR spectrum (400.0 MHz) of Complex **2c** in THF-*d8* at 20 °C.

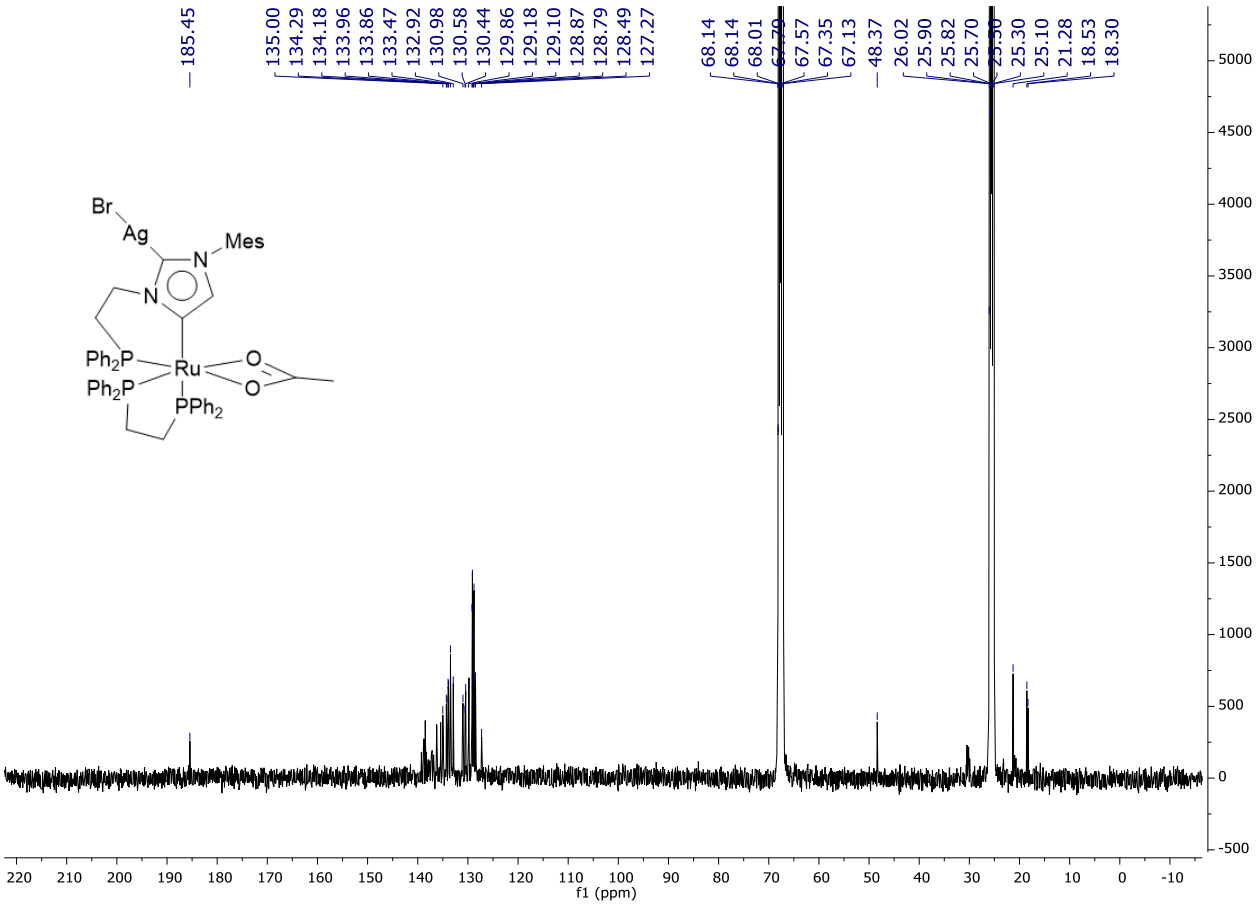

Figure S11. ^{13}C NMR spectrum (101.0 MHz) of Complex **2c** in THF-*d8* at 20 °C.

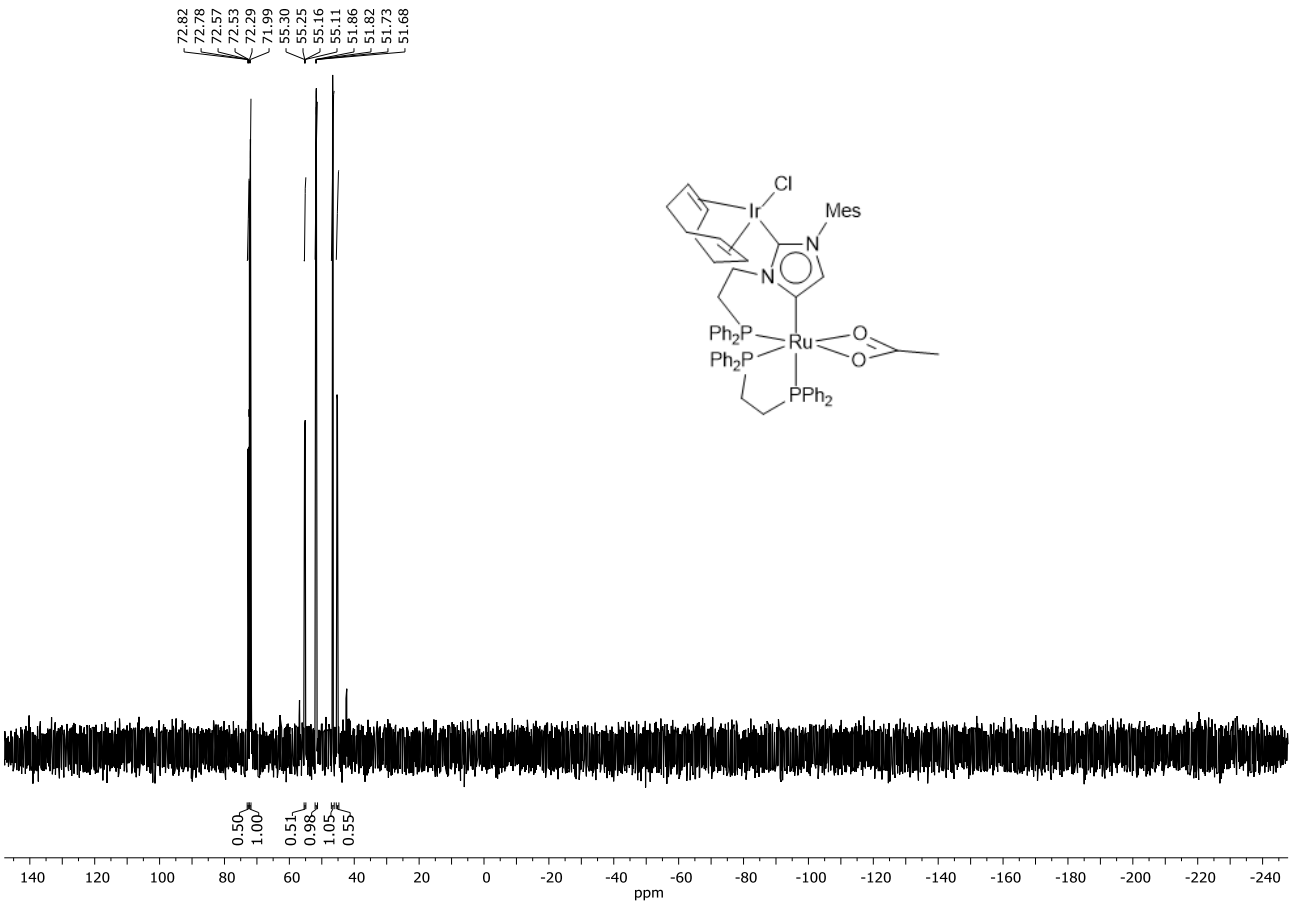

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (162.0 MHz) of Complex **2d** in CD_2Cl_2 at 20 °C.

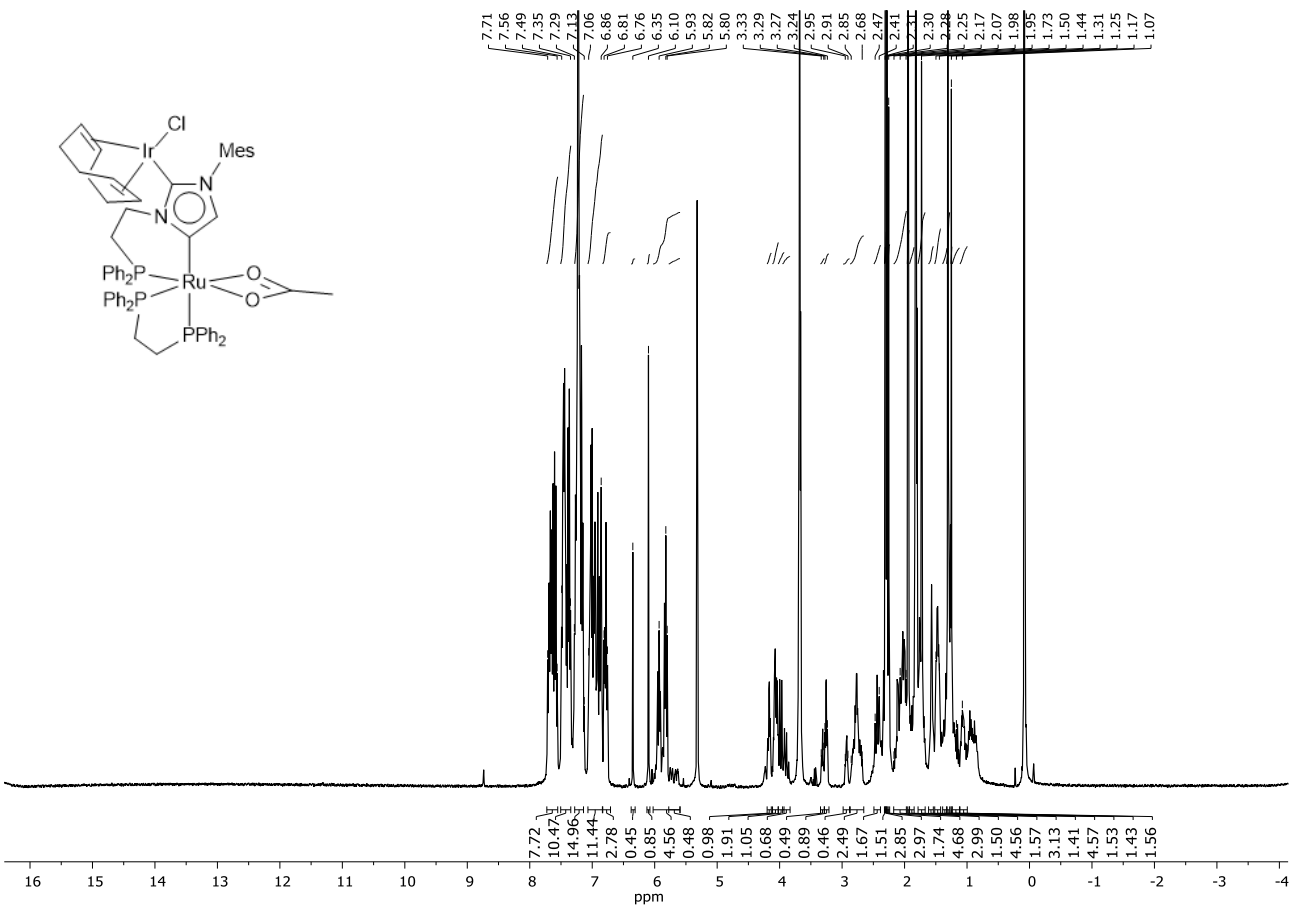

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (400.0 MHz) of Complex **2d** in CD_2Cl_2 at 20 °C.

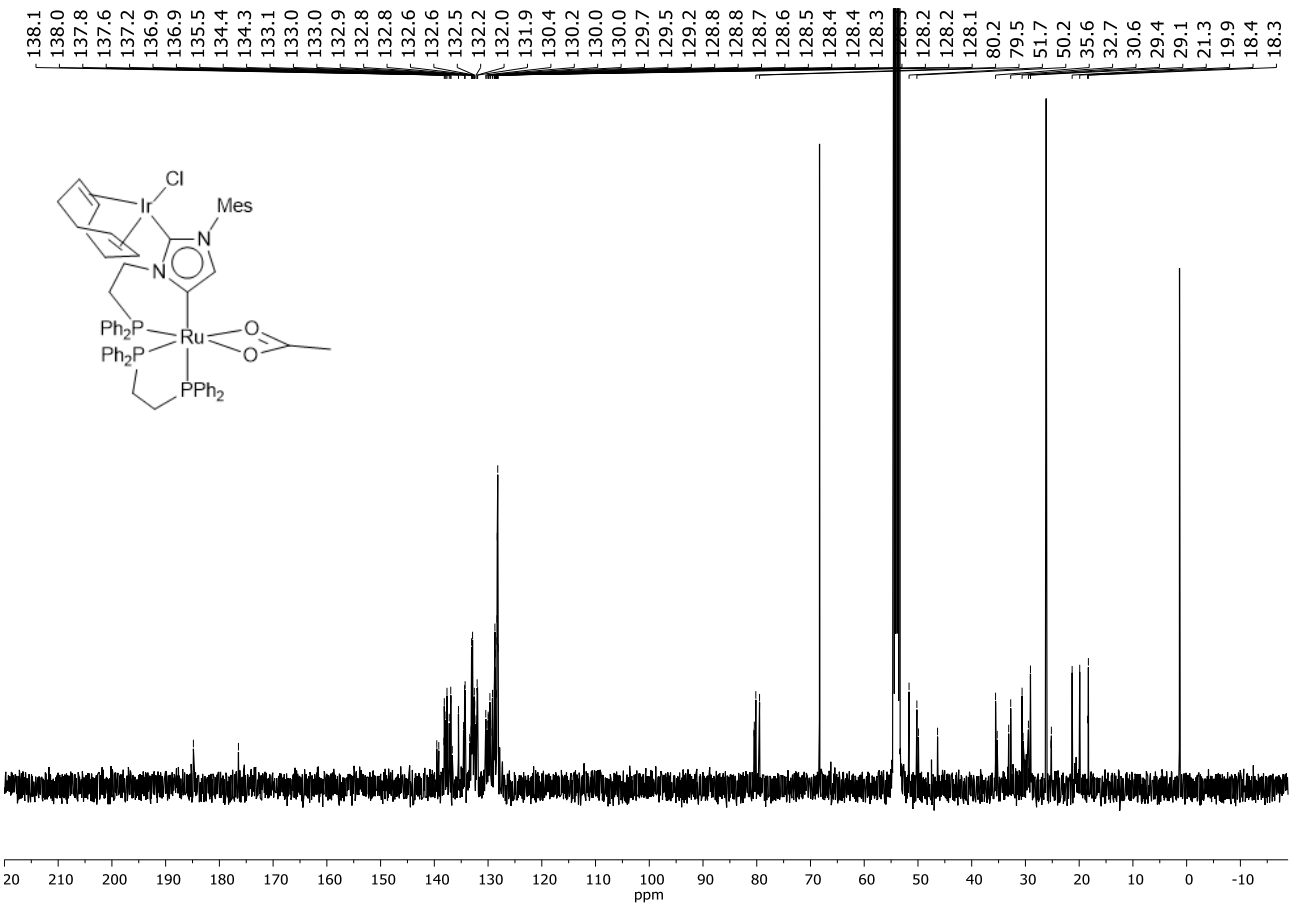

Figure S14. ^{13}C NMR spectrum (101.0 MHz) of Complex **2d** in CD_2Cl_2 at 20 °C.

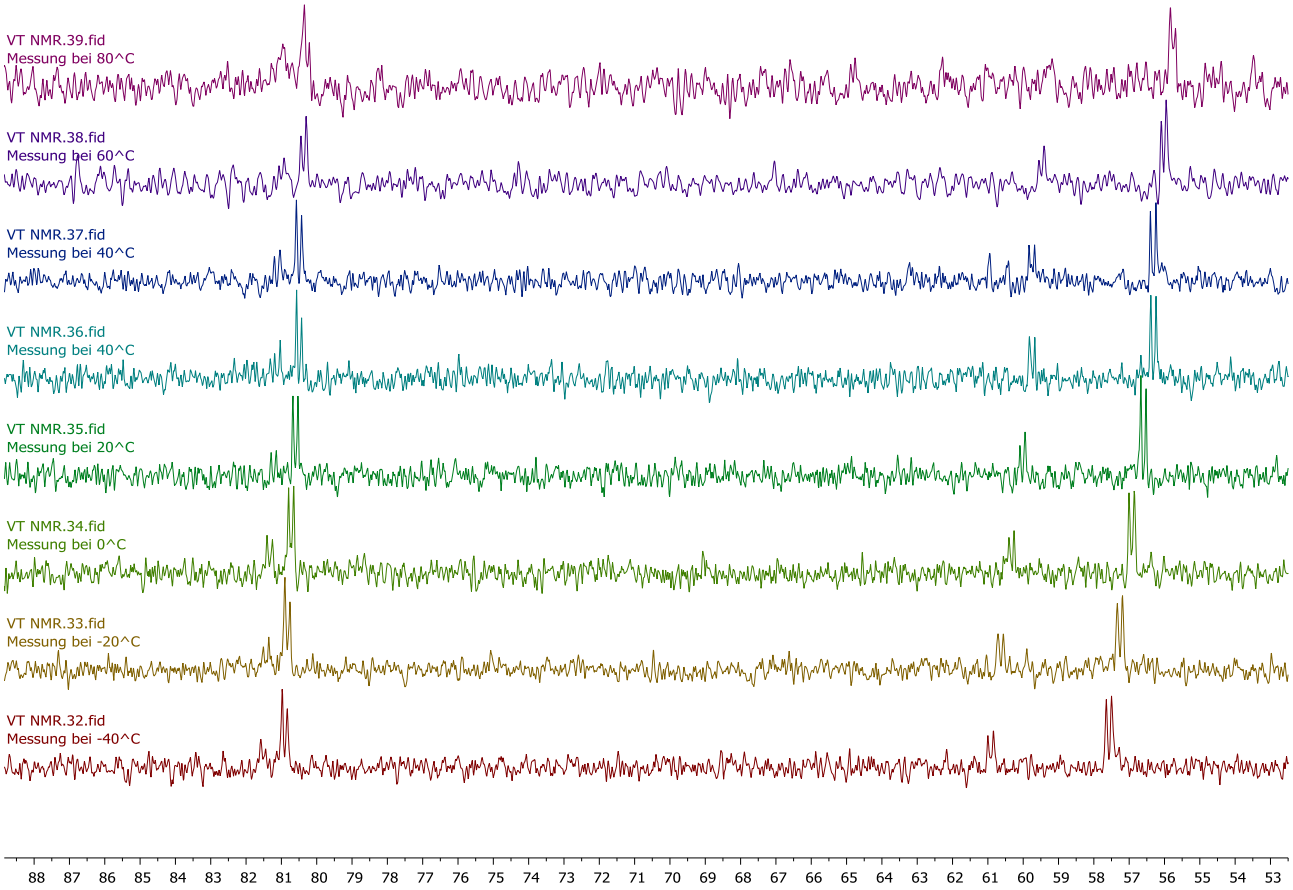

Figure S15. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra (162.0 MHz) of Complex **1e** in CD_2Cl_2 at 20 °C.

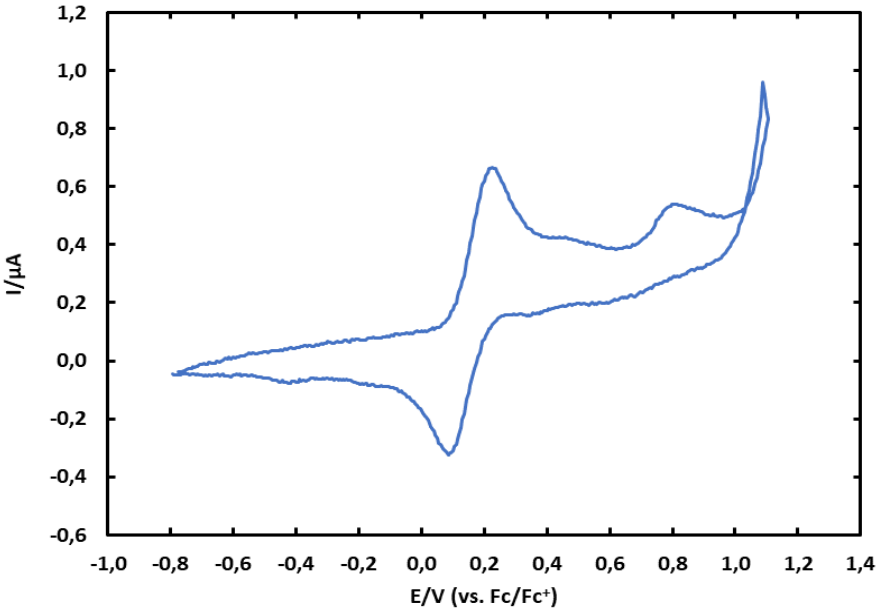

Figure S16. Cyclic Voltammogram of Au-Ru complex **1c**.

Single crystal X-Ray structure determination. General data.

X-ray crystallographic data were collected on different single crystal x-ray diffractometers with the following setups: [1]

1) a CCD detector (Bruker APEX II, κ-CCD), an FR591 rotating anode and a MONTEL mirror optic using the APEX2 software package (**1e**)

2) a CCD detector (Bruker APEX II, κ-CCD), a fine-focus sealed tube and a Triumph monochromator using the APEX2 software package (**2c**)

3) a CMOS detector (Bruker APEX III, κ-CMOS), a TXS rotating anode and a Helios optic using the APEX3 software package (**2b**)

4) a CMOS detector (Bruker APEX III, κ-CMOS), an IMS microsource and a Helios optic using the APEX3 software package (**2d**)

All measurements used MoK_α radiation (λ = 0.71073 Å). The measurements were performed on single crystals coated with perfluorinated ether. The crystal was fixed on top of a glass fiber or kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[2] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods (SHELXS) or charge flipping (SHELXT) with the aid of successive difference Fourier maps, and were refined against all data using SHELXL-2014 in conjunction with SHELXLE.[3,4,5] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 F_c^2)^2$ with SHELXL weighting scheme.[3] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[6] A split layer refinement was used for the disordered acetate and dppe

ligand in the case of **2c** and the disordered Ir(cod)Cl-moiety in the case of **2d** and additional SIMU, DELU, RIGU and SAME restraints were employed to ensure convergence within chemically reasonable limits, if necessary. The unit cell of **2b** contains 4 molecules of tetrahydrofuran and the unit cell of **2c** contains 8 molecules of diethyl ether which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[7] Images of the crystal structures were generated with Mercury.[8] CCDC 1860098-1860101 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystal X-ray structure determination. Detailed crystallographic data.

Crystallographic Data of Complex 1e (CCDC 1860098)

Sample and Crystal Data

Chemical formula	$C_{62}H_{68}Cl_5IrN_4O_2P_2Ru$
Formula weight	1433.66 g mol^{-1}
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal size	0.035 mm × 0.204 mm × 0.240 mm
Crystal habit	Fluorescent intense orange plate
Crystal System	Triclinic
Space group	P –1
Unit cell dimensions	a = 10.8823(5) Å, b = 14.2847(7) Å, c = 20.7956(10) Å, α = 78.593(2) °, β = 81.810(2) °, γ = 70.502(2) °
Volume	2976.9(2) Å^3
Z	2

Density (calculated)	1.599 g cm^{-3}
Absorption coefficient	2.812 mm^{-1}
F(000)	1440

Data Collection and Structure Refinement	
Diffractometer	Bruker Kappa Apex II CCD
Radiation Source	FR591 rotating anode, Mo
Theta range for data collection	1.69 to 25.35 °
Index ranges	–12≤h≤13, –17≤k≤17, –25≤l≤25
Reflections collected	100492
Independent reflections	10875 [R(int) = 0.0345]
Coverage of independent reflections	99.8 %
Max. and min. transmission	0.9080 and 0.5520
Data / restraints / parameters	10875 / 0 / 701
Goodness-of-fit on F^2	1.043
Δ/σ_{max}	0.001
Final R indices (8880 data; I>2σ(I))	R_1 = 0.0269, wR_2 = 0.0682
Final R indices (all data)	R_1 = 0.0308, wR_2 = 0.0711
Largest diff. max. min.	1.44 and –0.96 $eÅ^{-3}$

Crystallographic Data of Complex 2b (CCDC 1860101)

Sample and Crystal Data	
Chemical formula	$C_{64.05}H_{74.12}BrN_2O_{4.51}P_3Ru$
Formula weight	1218.10 g mol^{-1}
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.149 mm × 0.209 mm × 0.230 mm
Crystal habit	Clear yellow fragment

Crystal System	Monoclinic
Space group	P 1 2_1/c 1
Unit cell dimensions	*a* = 11.7840(15) Å, *b* = 20.151(3) Å, *c* = 26.982(4) Å, α = 90 °, β = 102.446(8) °, γ = 90 °
Volume	6256.6(14) Å^3
Z	4
Density (calculated)	1.293 g cm^{-3}
Absorption coefficient	1.013 mm^{-1}
F(000)	2531

Data Collection and Structure Refinement

Diffractometer	Bruker Kappa Apex II CCD
Radiation Source	TXS rotating anode, Mo
Theta range for data collection	2.16 to 25.35 °
Index ranges	–14≤h≤14, –24≤k≤24, –32≤l≤32
Reflections collected	121874
Independent reflections	11452 [R(int) = 0.0491]
Coverage of independent reflections	99.9 %
Max. and min. transmission	0.8640 and 0.8000
Data / restraints / parameters	11452 / 180 / 710
Goodness-of-fit on F^2	1.052
Δ/σ_{max}	0.001
Final R indices (8880 data; I>2σ(I))	R_1 = 0.0383, wR_2 = 0.1074
Final R indices (all data)	R_1 = 0.0440, wR_2 = 0.1118
Largest diff. max. min.	1.204 and –0.880 eÅ^{-3}

Crystallographic Data of Complex 2c (CCDC 1860099)

Sample and Crystal Data

Chemical formula	$C_{54}H_{53}AgBrN_2O_2P_3Ru$
Formula weight	1143.74 g mol^{-1}
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.263 mm × 0.330 mm × 0.432 mm
Crystal habit	Clear yellow fragment
Crystal System	Monoclinic
Space group	P 1 2_1/c 1
Unit cell dimensions	*a* = 15.193(3) Å, *b* = 14.891(3) Å, *c* = 26.067(4) Å, *α* = 90 °, *β* = 92.246(8) °, *γ* = 90 °
Volume	5893(2) $Å^3$
Z	4
Density (calculated)	1.289 g cm^{-3}
Absorption coefficient	1.384 mm^{-1}
F(000)	2312

Data Collection and Structure Refinement

Diffractometer	Bruker D8 Kappa Apex II
Radiation Source	Fine-focus sealed tube, Mo
Theta range for data collection	1.92 to 25.02 °
Index ranges	-18≤h≤18, -17≤k≤17, -31≤l≤31
Reflections collected	93474
Independent reflections	10401 [R(int) = 0.0394]
Coverage of independent reflections	100.0 %
Max. and min. transmission	0.7120 and 0.5860
Data / restraints / parameters	10401 / 488 / 764
Goodness-of-fit on F^2	1.037
Δ/σ_{max}	0.001
Final R indices (8880 data; I>2σ(I))	R_1 = 0.0447, wR_2 = 0.1283
Final R indices (all data)	R_1 = 0.0534, wR_2 = 0.1352

Largest diff. max. min.	0.821 and –2.364 eÅ^{-3}

Crystallographic Data of Complex 2d (CCDC 1860100)

Sample and Crystal Data

Chemical formula	$C_{62}H_{65}ClIrN_2O_2P_3Ru$
Formula weight	1291.79 g mol^{-1}
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.094 mm × 0.225 mm × 0.256 mm
Crystal habit	Clear yellow fragment
Crystal System	Triclinic
Space group	P –1
Unit cell dimensions	*a* = 12.0683(8) Å, *b* = 13.5766(10) Å, *c* = 18.7301(13) Å, *α* = 76.489(2) °, *β* = 83.192(2) °, *γ* = 77.258(2) °
Volume	2903.2(4) Å^3
Z	2
Density (calculated)	1.478 g cm^{-3}
Absorption coefficient	2.722 mm^{-1}
F(000)	1300

Data Collection and Structure Refinement

Diffractometer	Bruker D8 Venture Duo IMS
Radiation Source	IMS microsource, Mo
Theta range for data collection	2.24 to 26.02 °
Index ranges	–14≤h≤14, –16≤k≤16, –23≤l≤23

Reflections collected	100821
Independent reflections	11416 [R(int) = 0.0408]
Coverage of independent reflections	99.9 %
Max. and min. transmission	0.7840 and 0.5430
Data / restraints / parameters	11416 / 375 / 744
Goodness-of-fit on F^2	1.091
Δ/σ_{max}	0.001
Final R indices (8880 data; I>2σ(I))	R_1 = 0.0340, wR_2 = 0.0772
Final R indices (all data)	R_1 = 0.0389, wR_2 = 0.0799
Largest diff. max. min.	2.274 and –1.036 eÅ^{-3}

Single crystal X-ray structure determination. References.

1. *APEX suite of crystallographic software*, APEX 2, Version 2014-9.0 and APEX 3, Version 2015-5.2, Bruker AXS Inc., Madison, Wisconsin, USA, 2014/2015.
2. *SAINT*, Versions 8.34A and 8.37A and *SADABS*, Versions 2014/5 and 2016/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2014/2016.
3. Sheldrick, G. M. *Acta Cryst. C* **2015**, *71*, 3–8.
4. Sheldrick, G. M. *Acta Cryst. A* **2015**, *71*, 3–8.
5. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Cryst.* **2011**, *44*, 1281–1284
6. *International Tables for Crystallography*; A. J. Wilson, Ed.; Kluwer Academic Publishers: Dordrecht, The Nederlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500–502), 4.2.6.8 (pp 219–222), and 4.2.4.2 (pp 193–199).
7. Spek, A. L. *Acta Cryst. C* **2015**, *71*, 9–18.
8. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41*, 466–470.