Supporting Information

for

Platinum(II) as an assembly point for carbide and nitride ligands

Anders Reinholdt*[a] and Jesper Bendix*[a]

[a] *Department of Chemistry, University of Copenhagen*
Universitetsparken 5, DK-2100 Copenhagen (Denmark)
E-mail: a.reinholdt@chem.ku.dk, bendix@kiku.dk

2: Synthesis and Materials

$(Cy_3P)_2Cl_2Ru{\equiv}C$ (**RuC**),[1] *trans*-$[PtCl_2(C_2H_4)]_2$,[2] and $(dbm)_2Cr{\equiv}N$ (**CrN**)[3] were synthesized according to published procedures. Isotopically labelled $(Cy_3P)_2Cl_2Ru{\equiv}^{13}C$ was synthesized using CH_3CO_2–^{13}CH=$^{13}CH_2$ (Sigma-Aldrich, 99% ^{13}C). Dichloromethane (technical, VWR Chemicals), diethyl ether (technical, VWR Chemicals), heptane (technical, VWR Chemicals), pentane (Sigma-Aldrich, ≥99.0%), petroleum ether (40 – 65 °C, VWR Chemicals), and pyridine (Riedel-de Häen, min. 99.5%) were purchased from commercial suppliers and used as received.

Elemental analyses were carried out by the microanalytical services of the Department of Chemistry, University of Copenhagen using a FlashEA 1112 instrument.

Synthesis of $(Cy_3P)_2Cl_2Ru{\equiv}C$–$PtCl_2$–$N{\equiv}Cr(dbm)_2$ ($^{RuC}Pt^{NCr}$). *trans*-$[PtCl_2(C_2H_4)]_2$ (6.9 mg, 11.7 µmol) and **RuC** (17.5 mg, 23.5 µmol) were dissolved in 5 ml dichloromethane and heated to reflux temperature for 10 minutes. **CrN** (12.0 mg, 23.4 µmol) was added, resulting in an immediate color change from light orange to dark orange. The solution was stirred for 10 minutes, diluted with 10 ml heptane, and left to evaporate slowly at room temperature. After five days, red crystals of $(Cy_3P)_2Cl_2Ru{\equiv}C$–$PtCl_2$–$N{\equiv}Cr(dbm)_2$ (**$^{RuC}Pt^{NCr}$**) were separated from the mother liquor by centrifugation, washed with petroleum ether (40 – 65 °C, 3 x 3 ml), and air-dried. Yield of **$^{RuC}Pt^{NCr}$**: 31.5 mg, 20.7 µmol, 88.0% based on **RuC**. Elemental analysis, calculated for $C_{67}H_{88}Cl_4CrNO_4P_2PtRu$: C: 52.83%, H, 5.82%, N: 0.92%; found: C: 52.64%, H: 6.08%, N, 1.05%.

Synthesis of $(Cy_3P)_2Cl_2Ru{\equiv}^{13}C$–$PtCl_2$–$N{\equiv}Cr(dbm)_2$. Isotopically labelled **$^{RuC}Pt^{NCr}$** was prepared with $(Cy_3P)_2Cl_2Ru{\equiv}^{13}C$ replacing **RuC**.

The above procedure produces crystals suitable for X-ray crystallography (3 **$^{RuC}Pt^{NCr}$** in the asymmetric unit). Alternatively, the dichloromethane solution obtained after addition of **CrN** can be subjected to vapor diffusion (diethyl ether or pentane) to afford crystals of **$^{RuC}Pt^{NCr}$** · 2 CH_2Cl_2 (1 **$^{RuC}Pt^{NCr}$** in the asymmetric unit).

3: Crystallographic Details

X-ray crystallographic studies were carried out on single crystals of $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ coated with mineral oil and mounted on a nylon loop, which was transferred to the nitrogen cold stream of the diffractometer. The X-ray diffraction studies were performed at 120(2) K on a Bruker D8 VENTURE diffractometer equipped with a Mo $K\alpha$ high-brilliance IμS S3 radiation source (λ = 0.71073 Å), a multilayer X-ray mirror and a PHOTON 100 CMOS detector, and an Oxford Cryosystems low temperature device. The instrument was controlled with the APEX2 software package using SAINT.[4] Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS.[5] The structures were solved in Olex2 using the olex2.solve[6] program (Charge Flipping) and refined using SHELXL.[7] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters (U_{iso} = 1.2 U_{eq} of the parent atom for CH_2 and CH groups). In the small-unit-cell polymorph of $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$, disorder in a dichloromethane molecule was modelled using the SADI restraint. In the large-unit-cell polymorph of $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$, the ISOR restraint was applied to a few selected prolate C atoms; moreover, diffuse electron density in solvent accessible regions was modelled with the *use solvent mask* option in Olex2 (857.2 $Å^3$ with estimated electron counts of 14.5; CH_2Cl_2: 42 electrons). Selected crystallographic details are listed in **Tables S1 and S2**. CCDC entries 1913401 – 1913402 contain the crystallographic data reported herein. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Table S1. Crystallographic data for $(Cy_3P)_2Cl_2Ru{\equiv}C–PtCl_2–N{\equiv}Cr(dbm)_2$ ($^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$) polymorphs.

CCDC entry	**1913401**	**1913402**
Empirical formula	$C_{69}H_{92}Cl_8CrNO_4P_2PtRu$	$C_{67}H_{88}Cl_4CrNO_4P_2PtRu$
Formula weight	1693.13	1523.28
T / K	120(2)	120(2)
Crystal system	triclinic	triclinic
Space group	*P*–1	*P*–1
a / Å	13.8990(5)	13.9110(6)
b / Å	14.2368(5)	23.2724(10)
c / Å	18.9706(7)	32.5218(13)
α / °	86.8201(13)	88.0019(15)
β / °	88.6083(13)	78.0480(14)
γ / °	73.9461(12)	82.9501(14)
V / $Å^3$	3601.7(2)	10222.1(7)
Z	2	6
ρ_{calc} / g cm^{-3}	1.561	1.485
μ / mm^{-1}	2.68	2.672
F(000)	1714	4638.0
Crystal size / mm^3	0.146 × 0.051 × 0.041	0.537 × 0.108 × 0.079
Radiation	Mo $K\alpha$ (λ = 0.71073)	Mo $K\alpha$ (λ = 0.71073)
2θ range for data collection / °	4.816 – 52.744	4.336 – 50.054
Index ranges	$-17 \le h \le 17$, $-17 \le k \le 17$, $-23 \le l \le 23$	$-16 \le h \le 16$, $-27 \le k \le 27$, $-38 \le l \le 38$
Reflections collected	95397	325959
Independent reflections	14720 [R_{int} = 0.0360, R_{sigma} = 0.0209]	36120 [R_{int} = 0.0910, R_{sigma} = 0.0429]
Data / restraints / parameters	14720 / 6 / 841	36120 / 78 / 2216
Goodness-of-fit on F^2	1.042	1.047
Final *R* indexes [$I \ge 2\sigma (I)$]	R_1 = 0.0210, wR_2 = 0.0447	R_1 = 0.0423, wR_2 = 0.0953
Final *R* indexes [all data]	R_1 = 0.0255, wR_2 = 0.0465	R_1 = 0.0654, wR_2 = 0.1025
Largest diff. peak/hole / e $Å^{-3}$	0.83 / –0.69	2.27 / –1.12

Table S2. Metric data (Å, °) for ^{RuC}**Pt**^{NCr} polymorphs.

Molecule	**Ru–C**	**Cr–N**	**Pt–N**	**Pt–C**	**C–Pt–N**	**Ru–C–Pt**	**Cr–N–Pt**
1 ^{RuC}**Pt**^{NCr} per asymmetric unit (**1913401**)							
1	1.676(2)	1.579(2)	2.005(2)	1.899(2)	175.35(9)	174.5(1)	169.9(1)
3 ^{RuC}**Pt**^{NCr} per asymmetric unit (**1913402**)							
A	1.675(5)	1.584(5)	2.002(5)	1.909(5)	179.4(2)	178.0(3)	163.0(3)
B	1.677(5)	1.583(5)	1.990(5)	1.896(5)	179.7(2)	178.3(3)	169.2(3)
C	1.676(5)	1.583(5)	1.988(4)	1.906(5)	177.0(2)	175.5(3)	168.7(3)

4: Bond Distance Histograms

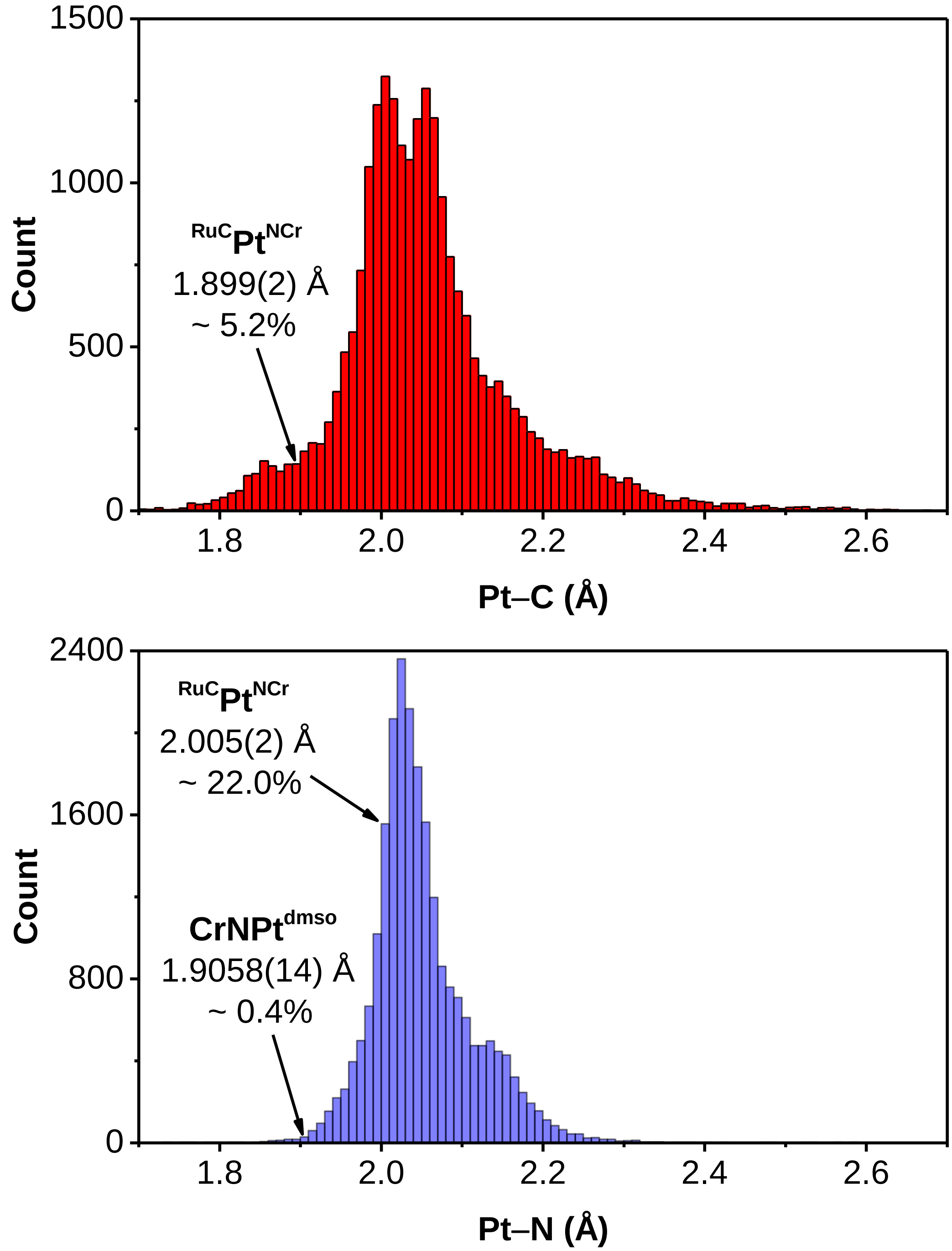


Figure S1. Histograms representing Pt–C (top) and Pt–N (bottom) bond distances (CSD v. 1.19). Bond distances with corresponding cumulative probabilities are indicated for $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ and $\mathbf{CrNPt}^{\mathbf{dmso}}$.

5: ESR Data

X-band ESR spectra were recorded on a Bruker Elexsys E500 ESR instrument equipped with X- and Q-band bridges. The experiments were carried out at room temperature using quartz tubes containing dichloromethane solutions. The ESR spectra were simulated with a Lorentzian lineshape (FWHH = 2.45 G) using the program SIM made available by H. Weihe. The constants, *c* and *v*, refer to the initial concentrations of **CrN** and **[RuCPt]**$_2$ (see **6: Equilibrium Constants**).

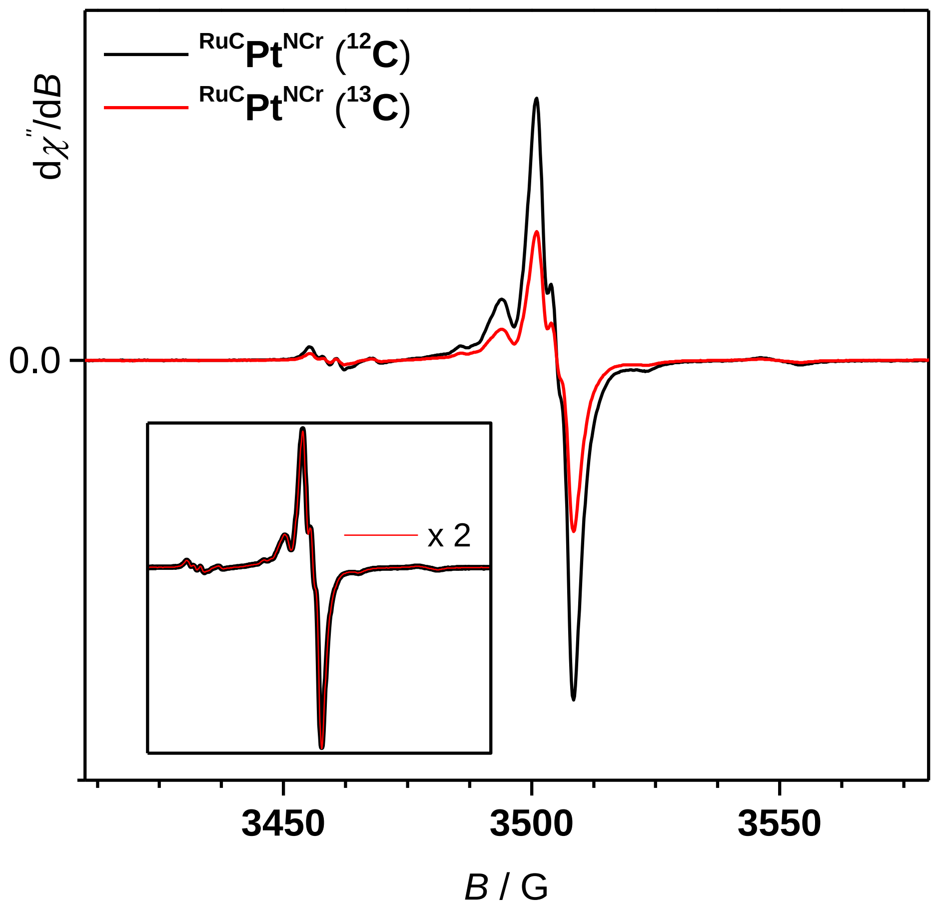


Figure S2. ESR spectra of crystalline $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ dissolved in CH_2Cl_2 (**RuC** precursor with a ^{13}C-labelled carbide ligand *versus* a natural isotope distribution). Each solution was prepared using 2.0 mg $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ in 2.0 ml CH_2Cl_2. [Formal concentration of $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$: 0.66 mM].

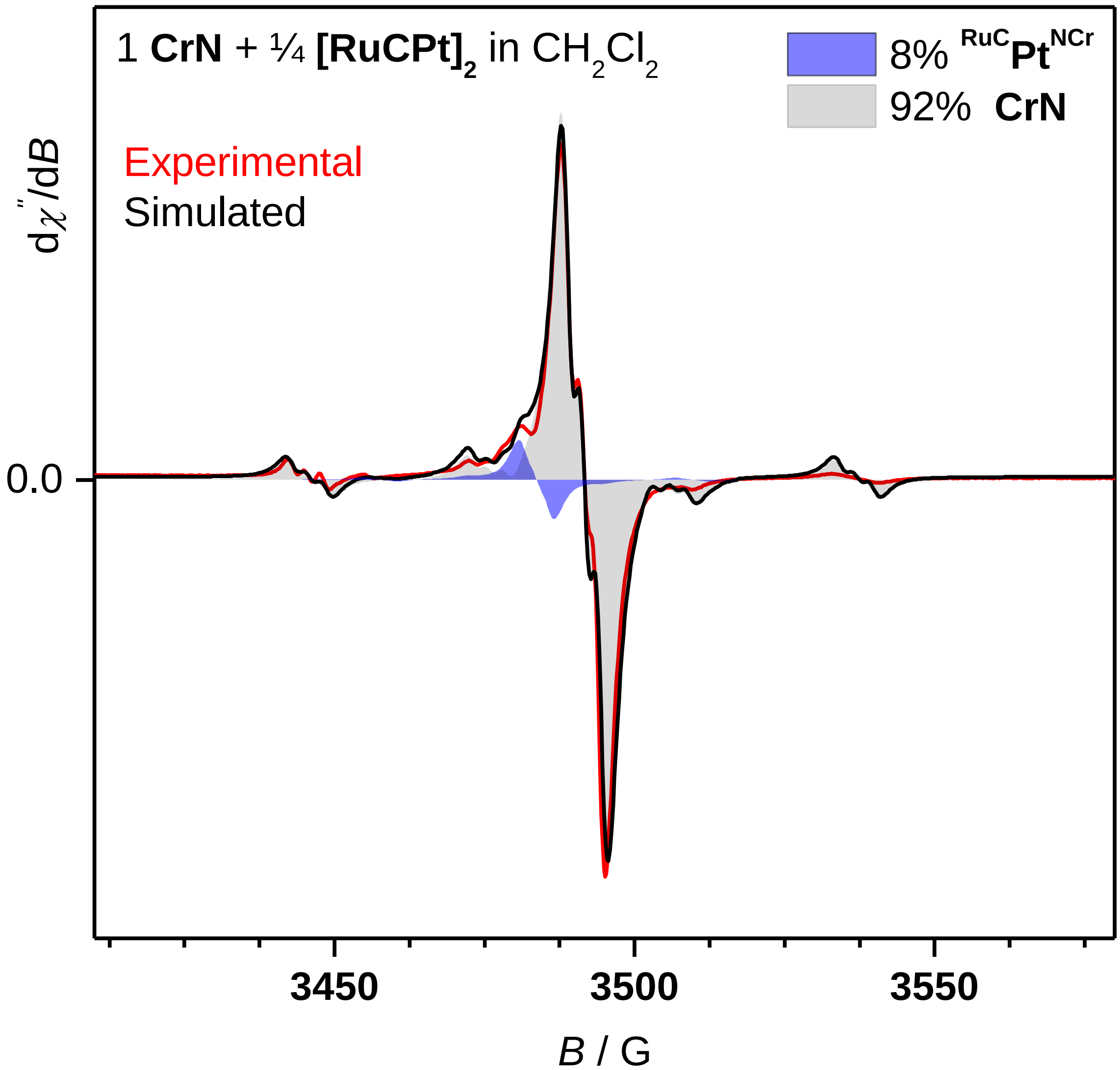


Figure S3. ESR spectrum of **^{RuC}Pt^{NCr}** reaction mixture [½ equivalent **RuC** per **CrN**]. The solution was generated from 7.4 mg **RuC** and 2.9 mg *trans*-[$PtCl_2(C_2H_4)$]$_2$ in 25 ml CH_2Cl_2. 10.3 mg **CrN** was added subsequently. [c = 0.80 mM and v = 0.20 mM].

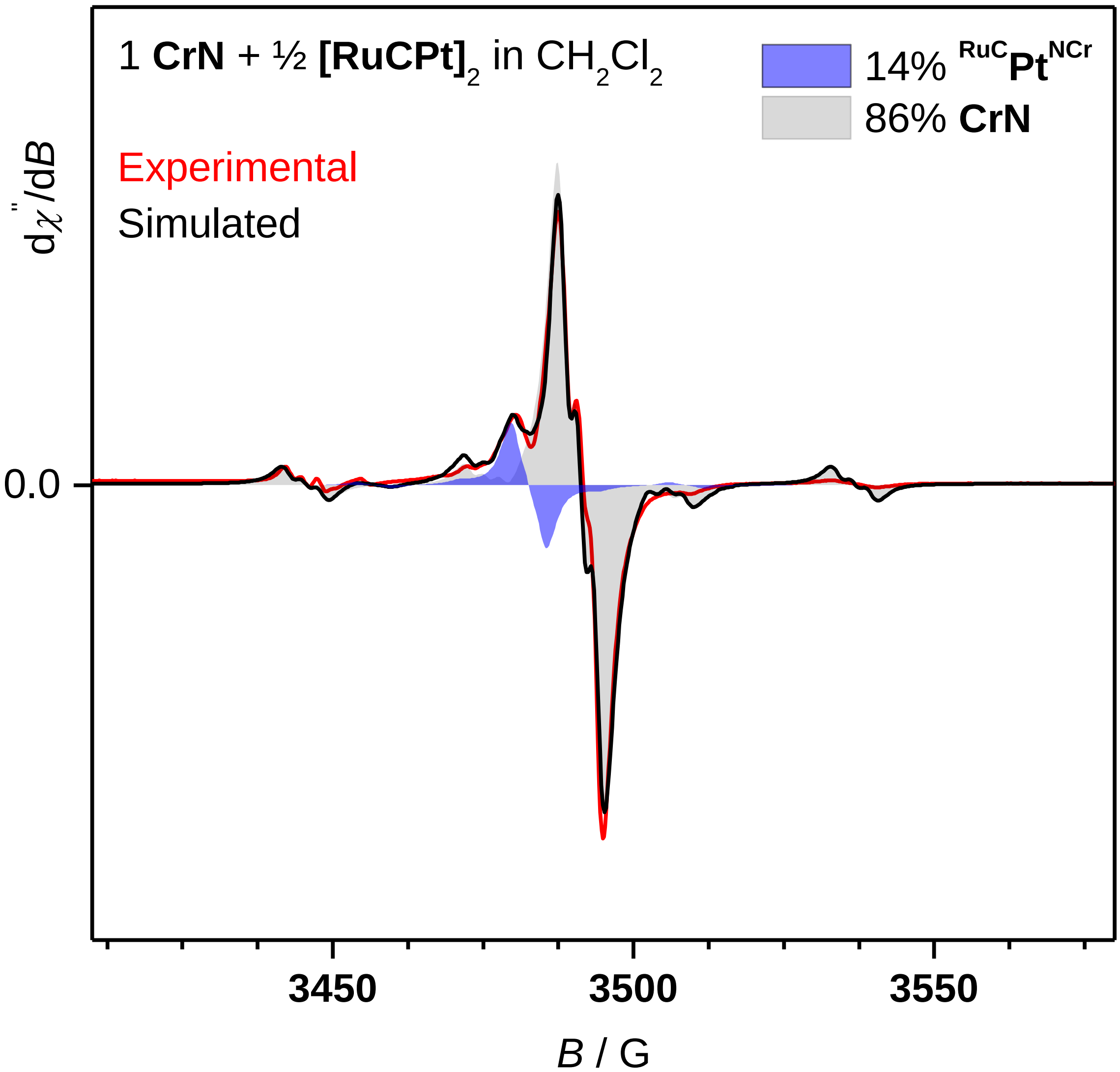


Figure S4. ESR spectrum of $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ reaction mixture [1 equivalent **RuC** per **CrN**]. The solution was generated from 14.9 mg **RuC** and 5.9 mg *trans*-$[PtCl_2(C_2H_4)]_2$ in 25 ml CH_2Cl_2. 10.3 mg **CrN** was added subsequently. [c = 0.80 mM and v = 0.40 mM].

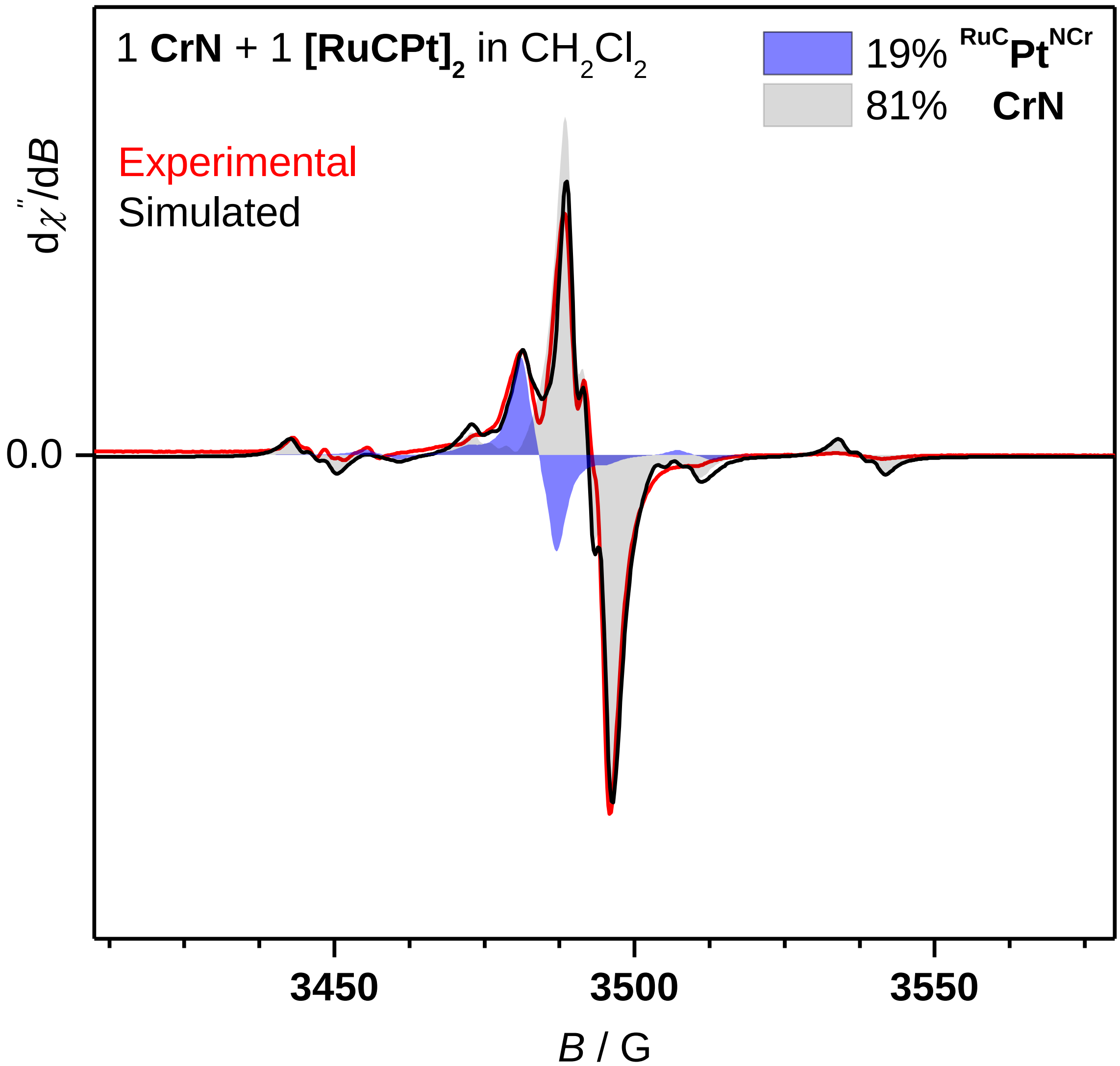


Figure S5. ESR spectrum of **^{RuC}Pt^{NCr}** reaction mixture [2 equivalents **RuC** per **CrN**]. The solution was generated from 29.8 mg **RuC** and 11.8 mg *trans*-[$PtCl_2(C_2H_4)]_2$ in 25 ml CH_2Cl_2. 10.3 mg **CrN** was added subsequently. [c = 0.80 mM and v = 0.80 mM].

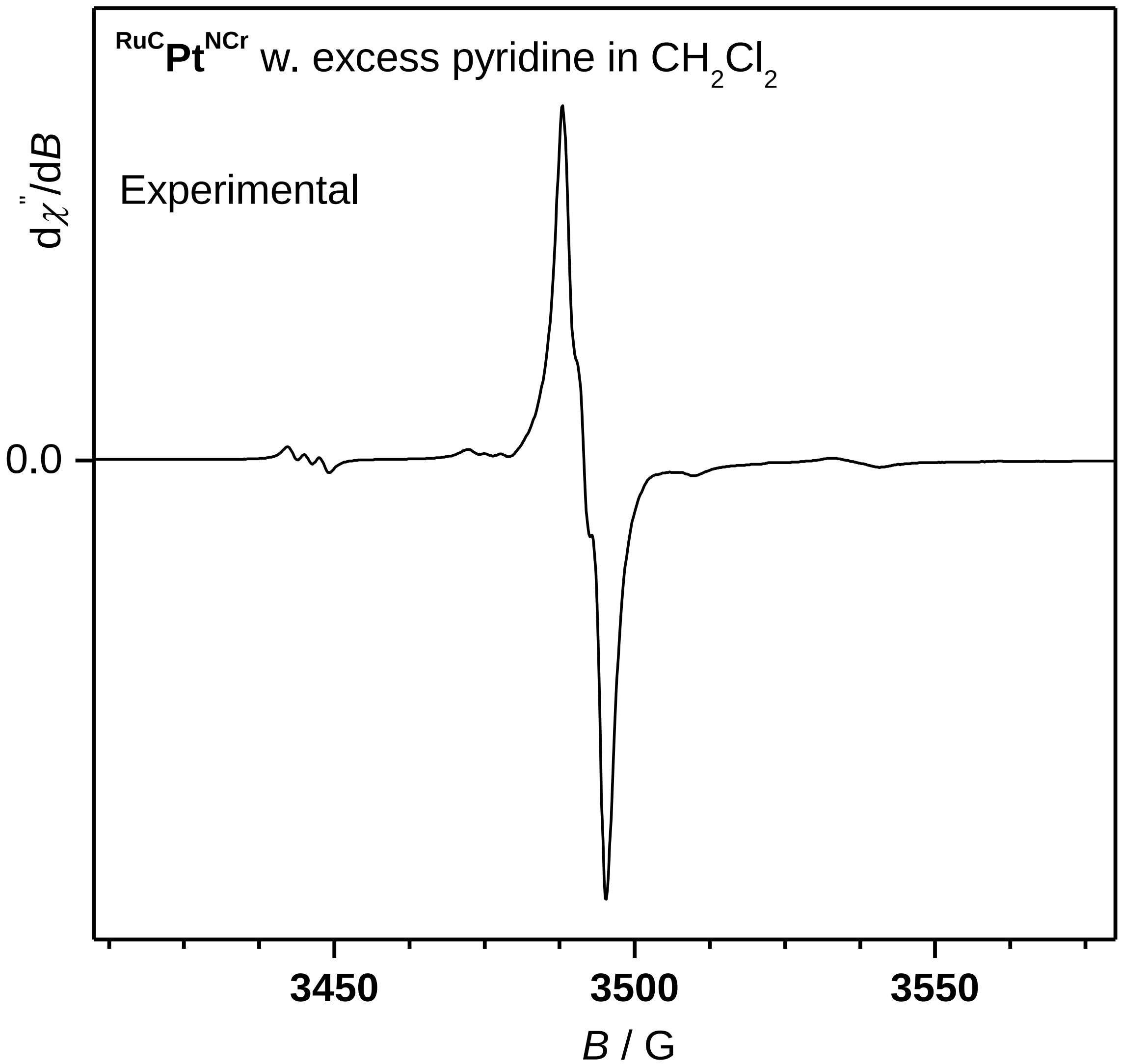


Figure S6. ESR spectrum of crystalline **^{RuC}Pt^{NCr}** dissolved in CH_2Cl_2 and subsequently treated with pyridine. *Only **CrN** was observed.*

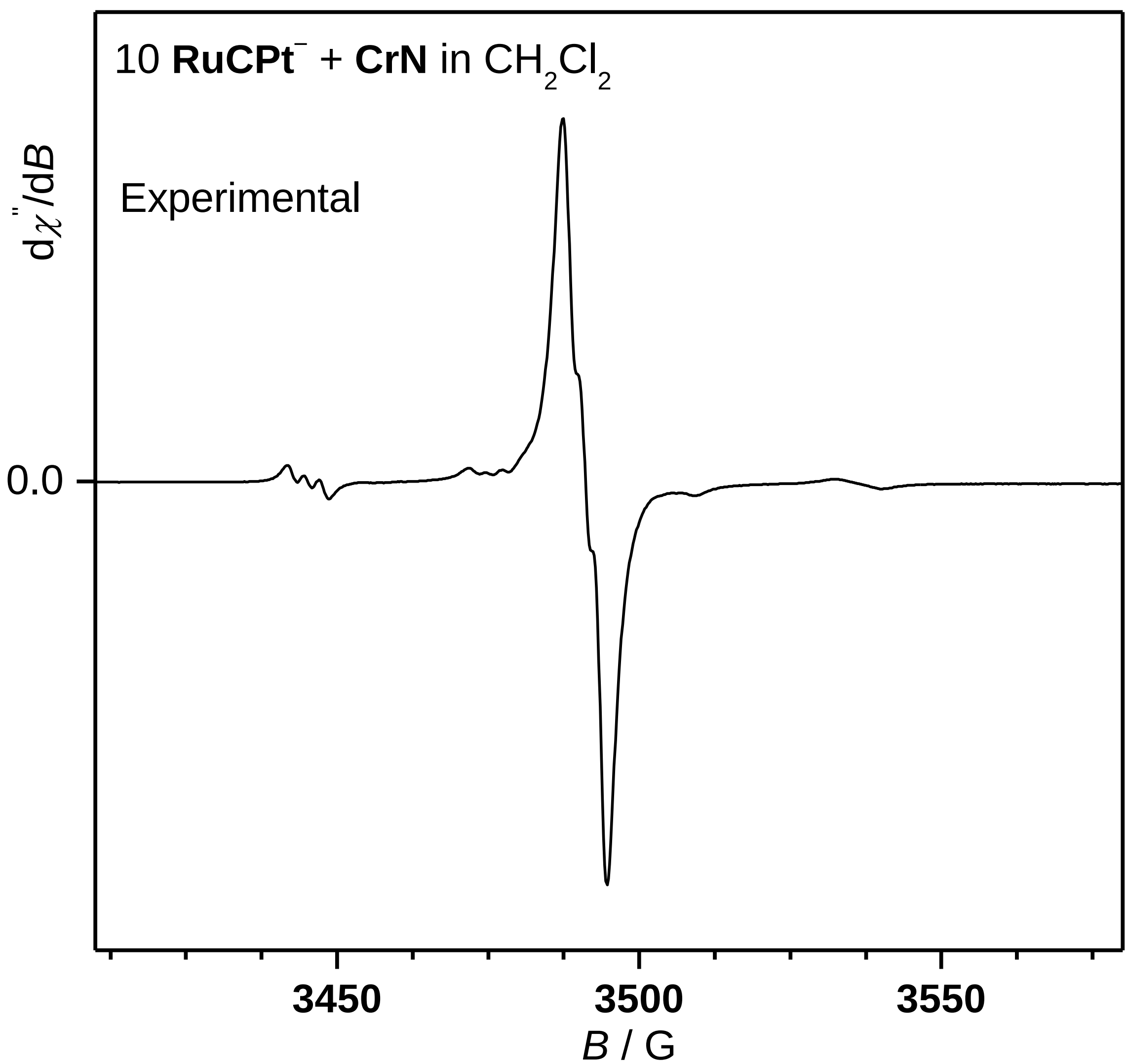
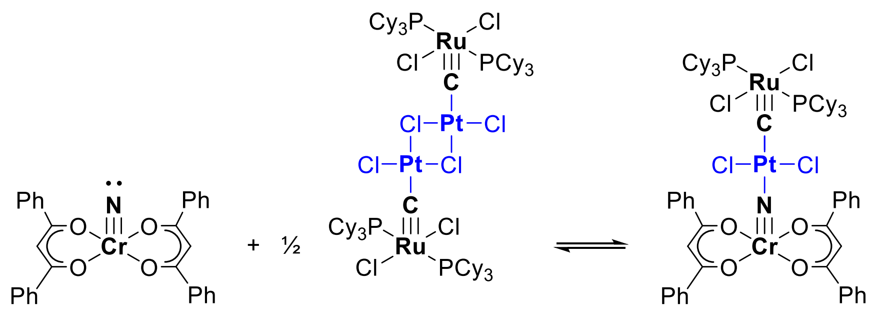


Figure S7. ESR spectrum of **RuCPt**⁻ treated with **CrN** [10 equivalents **RuC** per **CrN**]. A solution of **RuCPt**⁻ was generated from 14.3 mg $(AsPh_4)[PtCl_3(C_2H_4)]$ and 14.9 mg **RuC** in 2.4 ml CH_2Cl_2. 10.3 mg **CrN** was dissolved in 1.0 ml CH_2Cl_2, and an aliquot of 0.10 ml was added to the solution of **RuCPt**⁻. *Only* ***CrN*** *was observed.*

6: Equilibrium Constants

CrN and **[RuCPt]₂** (initial concentrations *c* and *v*, respectively) react to produce $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$:



CrN **[RuCPt]$_2$** $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$

initial	*c*	*v*	0
equilibrium	*c* – *x*	*v* – ½*x*	*x*

Scheme S1. Equilibrium between $^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$ and its precursors, **[RuCPt]$_2$** and **CrN**.

At equilibrium, the reaction has progressed by *x*, and the concentrations of nitride and carbide species are: [**CrN**] = *c* – *x*, [**[RuCPt]$_2$**] = *v* – ½*x*, [$^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}$] = *x*. The equilibrium constant, *K*, can be written:

$$K = \frac{\left[^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}} \right]}{[\mathbf{CrN}] \cdot \sqrt{[\mathbf{[RuCPt]_2}]}} = \frac{x}{(c-x)(v-\tfrac{1}{2}x)^{1/2}}$$

The ratio between chromium nitride complexes, $r = [^{\mathbf{RuC}}\mathbf{Pt}^{\mathbf{NCr}}] \cdot [\mathbf{CrN}]^{-1}$, can be determined from ESR spectroscopy. This quantity can be used to simplify *K*:

$$K = \frac{r}{\sqrt{v-\tfrac{1}{2}x}}$$

Moreover, $r = x \cdot (c - x)^{-1}$, can be rewritten:

$$x = \frac{rc}{1+r}$$

Thus, *K* can be expressed in terms of *c*, *v*, and *r*:

$$K = \frac{r}{\sqrt{v - \left(\frac{rc}{2(1+r)}\right)}}$$

From the ESR experiments, the following association constants (**Table S3**) emerge:

Table S3. Initial concentrations of **CrN** and **[RuCPt]$_2$** (*c* and *v*), ratio between **^{RuC}Pt^{NCr}** and **CrN** (*r*), and observed association constants (*K*).

Experiment	*c* / mM	*v* / mM	*r*	*K* / M$^{-½}$
½ **RuC** per **CrN**	0.80	0.20	0.087	6.7
1 **RuC** per **CrN**	0.80	0.40	0.16	8.8
2 **RuC** per **CrN**	0.80	0.80	0.23	8.7

7: References

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