

Supporting information

For

Delivering carbide moieties to sulfide-rich clusters

Anders Reinholdt,^a Konrad Herbst,^b Jesper Bendix^{a,*}

^a. *Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Denmark*

Telephone: +45 35320101; Email: bendix@kiku.dk

^b. *Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kongens Lyngby, Denmark*

| | |
|------------------------------|-----|
| Contents | S1 |
| Materials and methods | S2 |
| Syntheses | S3 |
| Physical measurements | S7 |
| Supporting figures | S10 |
| References | S24 |

Materials and methods

Unless otherwise stated, no precautions were taken to protect the reaction mixtures from air. Acetonitrile (Riedel-de Haën, >99.9%), chloroform (Sigma-Aldrich, HPLC, $\geq 99.8\%$), chloroform-*d* (Sigma-Aldrich, 99.8% D), dichloromethane (Sigma-Aldrich, HPLC, $\geq 99.8\%$), diethyl ether (VWR Chemicals), pentane (Sigma-Aldrich, HPLC, ≥ 99.0), and tetrabutylammonium hexafluorophosphate (Sigma-Aldrich, 98%) were purchased from commercial suppliers and used as received. Ru(C)Cl₂(PCy₃)₂ (**RuC**) was synthesized according to the published procedure;¹ **Ru**¹³C was obtained with ¹³CH₂¹³CH–O₂CCH₃ (Sigma-Aldrich, 99% ¹³C). [(MCp')₃S₄M'L]OTs (M = Mo or W, M'L = Pd(dba) or Pt(nor),^{2, 3} ttcn,⁴ [Cu(NCCH₃)₄]BF₄,⁵ [Ag(ttcn)]₄(OTf)₄,⁶ [AuCl(tht)],⁷ and (PNP)[(Cy₃P)₂Cl₂Ru≡C–PdCl₃]⁸ were prepared according to published procedures. [Ag(tht)₂]OTf (OTf⁻ replacing ClO₄⁻) was prepared by the obvious modification of the published procedure.⁹

Syntheses

[(Cy₃P)₂Cl₂Ru≡C–M'(MCp')₃S₄]OTs (1 – 4). General procedure for **1 – 4**. In the dark and under a nitrogen atmosphere, equimolar amounts of **RuC** and [(MCp')₃S₄M'L]OTs (typically 20 – 50 μmol) were dissolved in either CH₂Cl₂ or CHCl₃ (2 – 5 ml) and stirred until the formation of [(Cy₃P)₂Cl₂Ru≡C–M'(MCp')₃S₄]⁺ was complete. Typically, **1** and **3** require 3 hours of stirring at room temperature, **4** requires one day at room temperature, and **2** requires five days at refluxing temperature (CHCl₃). The Pd complexes **1** and **3** were isolated by adding diethyl ether to the reaction mixtures (typically five or ten-fold solvent volume) followed by several washings with diethyl ether, and drying *in vacuo*. Solutions of crude **2** were concentrated to 1 ml, and pentane vapour was allowed to diffuse into the solution, yielding dark needle crystals that were centrifuged off, washed with pentane and dried *in vacuo*. Crude **4** was evaporated to dryness, washed with pentane, and dried *in vacuo*. Yields 72 – 84%. Note: for the isolation of **1** and **3**, diethyl ether is preferred over pentane, as it readily dissolves dba, which colours the washings yellowish brown. X-ray-quality crystals of **1** and **3** were grown by diffusion of diethyl ether into chloroform solutions containing equal amounts of [(Cy₃P)₂Cl₂Ru≡C–Pd(MCp')₃S₄]OTs and (PNP)[(Cy₃P)₂Cl₂Ru≡C–PdCl₃] (PNP⁺ = bis(triphenylphosphoranylidene)iminium), affording the complex cations as their [(Cy₃P)₂Cl₂Ru≡C–PdCl₃][–] salts. X-ray-quality crystals of **2** and **4** were grown from chloroform by diffusion of pentane, affording the complex cations as their tosylate salts.

[(Cy₃P)₂Cl₂Ru≡C–Pd(MoCp')₃S₄]OTs (1). ¹H-NMR, 500 MHz, CDCl₃, δ: 7.83 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.74 (d, *J* = 1.8 Hz, 6H), 5.73 (d, *J* = 1.8 Hz, 6H), 2.67 – 2.51 (m, 6H), 2.31 (s, 3H), 2.11 – 2.03 (m, 12H), 2.02 (s, 9H), 1.94 – 1.85 (m, 12H), 1.83 – 1.76 (m, 6H), 1.56 – 1.44 (m, 12H), 1.35 – 1.22 (m, 18H). ¹³C-NMR, 126 MHz, CDCl₃, δ: 429.75, 144.78, 138.52, 128.43, 126.32, 115.70, 95.48, 93.81, 32.56 (t, *J* = 9.6 Hz), 30.51, 28.23 (t, *J* = 5.1 Hz), 26.76, 21.45, 15.68. ³¹P-NMR, 121 MHz, CDCl₃, δ: 35.53. ESI⁺ MS, CH₃CN, *m/z*, *f/c*: [(Cy₃P)₂Cl₂Ru≡C–Pd(MoCp')₃S₄]⁺ 1505.02 / 1504.98. Elemental analysis, calculated for C₆₂H₉₄Cl₂Mo₃O₃P₂PdRuS₅ · ¾ CHCl₃: C: 42.69%, H: 5.41%; found C: 42.72%, H: 5.25%.

[(Cy₃P)₂Cl₂Ru≡C–Pt(MoCp')₃S₄]OTs (2). ¹H-NMR, 500 MHz, CDCl₃, δ: 7.84 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 5.71 – 5.65 (m, 6H), 5.65 – 5.58 (m, 6H), 2.69 – 2.58 (m, 6H), 2.31 (s, 3H), 2.18 – 2.07 (m, 12H), 2.10 (s, 9H), 1.91 – 1.85 (m, 12H), 1.82 – 1.78 (m, 6H), 1.57 – 1.46 (m, 12H), 1.35 – 1.23 (m, 18H). ¹³C-NMR, 126 MHz, CDCl₃, δ: 385.41 (s and d, *J* = 2416.6 Hz), 144.72, 138.57, 128.45,

126.33, 114.97, 94.60, 93.06, 32.92 (t, $J = 9.4$ Hz), 30.65, 28.23 (t, $J = 4.5$ Hz), 26.72, 21.46, 15.61. ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 32.75. ESI⁺ MS, CH_3CN , m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pt}(\text{MoCp}')_3\text{S}_4]^+$ 1594.05 / 1593.04 (the carbide ligand was ^{13}C -labelled, explaining the m/z gain of 1). Elemental analysis, calculated for $\text{C}_{62}\text{H}_{94}\text{Cl}_2\text{Mo}_3\text{O}_3\text{P}_2\text{PtRuS}_5 \cdot \frac{3}{4} \text{CHCl}_3$: C: 40.65%, H: 5.15%; found C: 40.86%, H: 5.18%.

$[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pd}(\text{WCp}')_3\text{S}_4]\text{OTs}$ (3). ^1H -NMR, 300 MHz, CDCl_3 , δ : 7.84 (d, $J = 6.1$ Hz, 2H), 7.11 (d, $J = 7.1$ Hz, 2H), 5.91 – 5.83 (2 m, 12H), 2.66 – 2.49 (m, 6H), 2.32 (s, 3H), 2.21 (s, 9H), 2.16 – 1.99 (m, 12H), 1.98 – 1.85 (m, 12H), 1.85 – 1.73 (m, 6H), 1.60 – 1.42 (m, 12H), 1.36 – 1.23 (m, 18H). ^{13}C -NMR (126 MHz, Chloroform-*d*) δ 421.40, 144.83, 138.51, 128.44, 126.32, 114.60, 94.07, 91.44, 32.49 (t, $J = 9.5$ Hz), 30.55, 28.28, 26.82, 21.46, 15.63. ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 34.63. FAB⁺ MS, *m*-NBA, m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pd}(\text{WCp}')_3\text{S}_4]^+$ 1769.6 / 1769.12, $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pd}(\text{WCp}')_3\text{S}_4 - \text{PCy}_3]^+$ 1488.8 / 1488.88, $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pd}(\text{WCp}')_3\text{S}_4 - \text{PCy}_3 - \text{Cl}]^+$ 1453.1 / 1451.92, $[\text{Pd}(\text{WCp}')_3\text{S}_4]^+$ 1023.6 / 1022.81, $[(\text{WCp}')_3\text{S}_4]^+$ 917.0 / 916.91. Elemental analysis, calculated for $\text{C}_{62}\text{H}_{94}\text{Cl}_2\text{O}_3\text{P}_2\text{PdRuS}_5\text{W}_3 \cdot 1.5 \text{CHCl}_3$: C: 36.00%, H: 4.54%; found C: 36.10%, H: 4.25%.

$[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pt}(\text{WCp}')_3\text{S}_4]\text{OTs}$ (4). ^1H -NMR, 500 MHz, CDCl_3 , δ : 7.83 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 5.82 – 5.78 (m, 6H), 5.76 – 5.72 (m, 6H), 2.68 – 2.56 (m, 6H), 2.32 (s, 3H), 2.28 (s, 9H), 2.17 – 2.09 (m, 12H), 1.92 – 1.86 (m, 12H), 1.82 – 1.76 (m, 6H), 1.57 – 1.47 (m, 12H), 1.34 – 1.24 (m, 18H). ^{13}C -NMR, 126 MHz, CDCl_3 , δ : 378.15 (t, $J = 5.5$ Hz and d, $J = 2600.4$ Hz), 144.74, 138.59, 128.47, 126.31, 113.85, 93.09, 90.48, 32.83 (t, $J = 9.5$ Hz), 30.68, 28.27 (t, $J = 4.9$ Hz), 26.79, 21.46, 15.50. ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 31.97. FAB⁺ MS, *m*-NBA matrix, m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pt}(\text{WCp}')_3\text{S}_4]^+$ 1855.6 / 1857.18, $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Pt}(\text{WCp}')_3\text{S}_4 - \text{PCy}_3]^+$ 1574.2 / 1576.94, $[(\text{WCp}')_3\text{S}_4]^+$ 915.8 / 916.91. Elemental analysis, calculated for $\text{C}_{62}\text{H}_{94}\text{Cl}_2\text{O}_3\text{P}_2\text{PtRuS}_5\text{W}_3 \cdot \frac{1}{2} \text{CHCl}_3$: C: 35.95%, H: 4.56%; found C: 36.01%, H: 4.32%.

$[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Cu}(\text{ttcn})]\text{BF}_4$ (5). Under a nitrogen atmosphere, $[\text{Cu}(\text{NCCH}_3)_4]\text{BF}_4$ (13.8 mg, 43.9 μmol) and *ttcn* (7.9 mg, 44 μmol) were dissolved in 10 ml nitrogen-purged acetonitrile and heated to reflux temperature for one hour. During this time, the initially intense yellow colour faded to become nearly colourless. **RuC** (32.7 mg, 43.9 μmol) in 10 ml nitrogen-purged chloroform was added, and the solution was kept at reflux temperature for 15 minutes. The solvents were evaporated off, and the dry residue was dissolved in 1 ml chloroform. Diethyl ether vapour was allowed to diffuse into the solution over 2 days. Yellow crystals of $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Cu}(\text{ttcn})]\text{BF}_4$ (5) were decanted off, washed with

diethyl ether (2 x 2 ml), and dried *in vacuo*. Yield of **5**: 39.1 mg, 36.4 μmol , 82.8% based on **RuC**. ^1H -NMR, 500 MHz, CDCl_3 , δ : 3.14 – 3.01 (m, 6H), 2.85 – 2.75 (m, 6H), 2.74 – 2.60 (m, 6H), 2.19 – 2.05 (m, 12H), 1.87 – 1.78 (m, 12H), 1.78 – 1.72 (m, 6H), 1.60 – 1.48 (m, 12H), 1.34 – 1.17 (m, 18H). ^{13}C -NMR, 126 MHz, CDCl_3 , δ : 431.69, 32.41, 32.03 (t, $J = 9.9$ Hz), 30.26, 28.06 (t, $J = 5.2$ Hz), 26.54. ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 41.02. ^{19}F -NMR, 282 MHz, CDCl_3 , δ : –152.62. ESI⁺ MS, CH_3CN , m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Cu}(\text{ttcn})]^+$ 989.26 / 989.24. Elemental analysis, calculated for $\text{C}_{43}\text{H}_{78}\text{BCl}_2\text{CuF}_4\text{P}_2\text{RuS}_3$: C: 48.02%, H: 7.31%; found C: 47.85%, H: 7.34%.

$[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Ag}(\text{ttcn})]\text{OTf}$ (6**)**. $[\text{Ag}(\text{ttcn})]_4(\text{OTf})_4$ (10.2 mg, 5.83 μmol) and **RuC** (17.4 mg, 23.4 μmol) were dissolved in 5 ml chloroform and heated to reflux temperature for one hour. After filtering, the solvent was evaporated off, leaving a yellow residue of $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Ag}(\text{ttcn})]\text{OTf}$ that was washed with diethyl ether (3 x 5 ml), and dried *in vacuo*. Yield of **6** · $\frac{1}{3}$ CHCl_3 : 24.7 mg, 20.2 μmol , 86.5% based on **RuC**. ^1H -NMR, 300 MHz, CDCl_3 , δ : 3.30 – 3.07 (m, 6H), 2.84 – 2.59 (m, 12H), 2.23 – 2.04 (m, 12H), 1.94 – 1.69 (m, 18H), 1.69 – 1.47 (m, 12H), 1.40 – 1.19 (m, 18H). ^{13}C -NMR, 126 MHz, CDCl_3 , δ : 431.84 (d, $J = 175.4$ Hz), 120.81 (q, $J = 320.2$ Hz), 32.22 (t, $J = 9.9$ Hz), 30.30, 29.98, 28.07 (t, $J = 5.2$ Hz), 26.55. ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 42.28. ^{19}F -NMR, 282 MHz, CDCl_3 , δ : –78.72. ESI⁺ MS, CH_3CN , m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Ag}(\text{ttcn})]^+$ 1033.23 / 1033.22. Elemental analysis, calculated for $\text{C}_{44}\text{H}_{78}\text{AgCl}_2\text{F}_3\text{O}_3\text{P}_2\text{RuS}_4 \cdot \frac{1}{3} \text{CHCl}_3$: C: 43.58%, H: 6.46%; found C: 43.61%, H: 6.39%.

$[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Au}(\text{ttcn})]\text{OTf}$ (7**)**. $\text{AuCl}(\text{tht})$ (1.7 mg, 5.3 μmol) and $[\text{Ag}(\text{tht})_2]\text{OTf}$ (2.3 mg, 5.3 μmol) were dissolved in 0.3 ml CDCl_3 and stirred for 5 minutes, producing a white precipitate of AgCl . With an additional 0.3 ml CDCl_3 , ttcn (1.0 mg, 5.5 μmol) was added, and the solution was stirred for five minutes. Finally, **Ru**¹³**C** (4.0 mg, 5.4 μmol in 0.2 ml CDCl_3) was added, the solution was stirred for ten minutes and analysed by NMR. As **7** decomposes and occurs along with $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{AuCl}$ and tht , the most informative spectroscopic data are: ^{13}C -NMR, 126 MHz, CDCl_3 , δ : 414.12 (t, $J = 5.0$ Hz). ^{31}P -NMR, 121 MHz, CDCl_3 , δ : 40.70. ESI⁺ MS, CH_3CN , m/z , f/c : $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{Au}(\text{ttcn})]^+$ 1123.31 / 1123.28. For spectra, see Figures S10 – S14.

Conversion of **5 to **3****. Solid **5** (1.1 mg, 1.0 μmol) was dissolved in 0.5 ml CDCl_3 ; the ^1H -NMR and ^{31}P -NMR spectra showed only resonances from **5**. $[(\text{WCp}^*)_3\text{S}_4\text{Pd}(\text{dba})]\text{OTs}$ (1.4 mg, 0.98 μmol) was added to the solution. After 15 minutes, ^1H and ^{31}P NMR spectra showed only resonances from **5**. After 21 h,

resonances from **3** and **5** were visible, having the ratio 2:5 (by ^1H integrals, see Figure S15) and 1:3 (by ^{31}P integrals, see Figure S16).

Physical measurements

NMR-spectroscopy: $^{31}\text{P}\{^1\text{H}\}$ -NMR and ^{19}F -NMR spectra were recorded on a 300 MHz Varian instrument. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded on a 500 MHz Bruker instrument with a cryoprobe, and ^1H -NMR spectra were recorded on a 300 MHz Varian instrument or a 500 MHz Bruker instrument with a cryoprobe. ^1H and ^{13}C resonances were referenced to residual solvent signals (CDCl_3 : $\delta = 7.26$, ^1H , and 77.16 ppm, ^{13}C). ^{31}P and ^{19}F signals were referenced to the deuterium resonances arising from the solvents.

Mass spectrometric measurements were carried out on a Jeol four sector instrument (FAB, with *m*-nitrobenzylalcohol [*m*-NBA] as matrix) or on a Bruker Solarix XR ESI/MALDI FT-ICR MS instrument (ESI, acetonitrile containing formic acid as solvent).

Elemental analyses were performed by the microanalytical services of the Department of Chemistry, University of Copenhagen.

X-ray crystallographic studies employed single crystals of **1** – **6** that were coated with mineral oil, placed on nylon loops, and mounted in the nitrogen cold stream of the diffractometer. The single-crystal X-ray diffraction studies were performed at 122(2) K on a Bruker D8 VENTURE diffractometer equipped with a Mo $K\alpha$ high-brilliance $I\mu\text{S}$ radiation source ($\lambda = 0.71073 \text{ \AA}$), 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.¹⁰ 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.¹¹ The structures were solved in Olex2 using the olex2.solve¹² program (Charge Flipping) and refined using the olex2.refine program¹³ or SHELXL.¹⁴ All non-hydrogen atoms were refined anisotropically; in disordered fragments, the least occupant parts were refined isotropically, if necessary. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters ($U_{\text{iso}} = 1.2 U_{\text{eq}}$ of the parent atom, except for methyl hydrogens which were constrained to $1.5 U_{\text{eq}}$ of the parent atom). Disorder was treated with appropriate choices of the EADP, ISOR, and SADI commands. CCDC entries 1433236-1433241 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. Selected crystallographic details are listed in Table S1 below.

Table S1. Crystallographic data for **1 – 6**.

| | | | |
|---|--|---|---|
| Compound | 1 (CCDC 1433236) | 2 (CCDC 1433237) | 3 (CCDC 1433238) |
| Empirical formula | C _{95.19} H _{158.33} Cl _{11.82} Mo ₃ O _{0.40} P ₄ Pd ₂ Ru ₂ S ₄ | C ₆₅ H ₉₇ Cl ₁₁ Mo ₃ O ₃ P ₂ PtRuS ₅ | C _{94.65} H _{154.79} Cl _{12.35} O _{0.22} P ₄ Pd ₂ Ru ₂ S ₄ W ₃ |
| Formula weight | 2682.91 | 2122.59 | 2952.62 |
| Temperature / K | 122(2) | 122(2) | 122(2) |
| Crystal system | triclinic | monoclinic | triclinic |
| Space group | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> -1 |
| <i>a</i> / Å | 13.8281(9) | 22.0554(19) | 13.8702(4) |
| <i>b</i> / Å | 17.5883(11) | 9.9627(9) | 17.6143(5) |
| <i>c</i> / Å | 23.8941(16) | 36.388(3) | 23.8397(8) |
| α / ° | 80.217(2) | 90 | 80.2950(10) |
| β / ° | 75.331(2) | 93.738(2) | 75.2550(10) |
| γ / ° | 84.330(3) | 90 | 83.9490(10) |
| <i>V</i> / Å ³ | 5530.7(6) | 7978.5(12) | 5540.0(3) |
| <i>Z</i> | 2 | 4 | 2 |
| ρ_{calc} / g cm ⁻³ | 1.611 | 1.767 | 1.770 |
| μ / mm ⁻¹ | 1.374 | 2.972 | 4.156 |
| 2θ range for data collection / ° | 4.496 to 51.362 | 4.488 to 50.054 | 4.346 to 52.044 |
| Reflections collected | 125278 | 107771 | 84030 |
| Independent reflections | 20984 [<i>R</i> _{int} = 0.0605] | 14078 [<i>R</i> _{int} = 0.0701] | 21806 [<i>R</i> _{int} = 0.0423] |
| Restraints / parameters | 6 / 1132 | 56 / 884 | 8 / 1119 |
| Goodness-of-fit on <i>F</i> ² | 1.018 | 1.120 | 1.043 |
| Final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0314, <i>wR</i> ₂ = 0.0630 | <i>R</i> ₁ = 0.0553, <i>wR</i> ₂ = 0.1049 | <i>R</i> ₁ = 0.0359, <i>wR</i> ₂ = 0.0755 |
| Final <i>R</i> indexes [all data] | <i>R</i> ₁ = 0.0482, <i>wR</i> ₂ = 0.0686 | <i>R</i> ₁ = 0.0789, <i>wR</i> ₂ = 0.1117 | <i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.0839 |
| Largest diff. peak / hole / e Å ⁻³ | 2.24 / -1.83 | 2.19 / -1.24 | 3.40 / -2.14 |
| Compound | 4 (CCDC 1433239) | 5 (CCDC 1433240) | 6 (CCDC 1433241) |
| Empirical formula | C ₆₅ H ₉₇ Cl ₁₁ O ₃ P ₂ PtRuS ₅ W ₃ | C ₄₇ H _{86.5} BCl ₅ CuF ₄ O _{0.75} P ₂ RuS ₃ | C _{46.92} H _{84.77} AgCl _{3.08} F ₃ O _{3.64} P ₂ RuS ₄ |
| Formula weight | 2386.32 | 1250.45 | 1272.44 |
| Temperature / K | 122(2) | 122(2) | 122(2) |
| Crystal system | monoclinic | triclinic | orthorhombic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> -1 | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> / Å | 22.1025(17) | 9.636(3) | 9.5010(4) |
| <i>b</i> / Å | 9.9658(8) | 17.256(5) | 22.3773(10) |
| <i>c</i> / Å | 36.424(3) | 18.491(7) | 27.2642(11) |
| α / ° | 90 | 91.100(14) | 90 |
| β / ° | 93.775(2) | 97.986(16) | 90 |
| γ / ° | 90 | 99.976(12) | 90 |
| <i>V</i> / Å ³ | 8005.8(11) | 2995.8(16) | 5796.6(4) |
| <i>Z</i> | 4 | 1 | 4 |
| ρ_{calc} / g cm ⁻³ | 1.980 | 1.386 | 1.458 |
| μ / mm ⁻¹ | 6.799 | 1.032 | 0.987 |
| 2θ range for data collection / ° | 4.594 to 50.054 | 4.454 to 55.756 | 4.54 to 50.054 |
| Reflections collected | 119943 | 42665 | 61707 |
| Independent reflections | 14116 [<i>R</i> _{int} = 0.0985] | 14016 [<i>R</i> _{int} = 0.0327] | 10245 [<i>R</i> _{int} = 0.1039] |
| Restraints / parameters | 14 / 839 | 42 / 703 | 60 / 633 |
| Goodness-of-fit on <i>F</i> ² | 1.118 | 1.030 | 1.051 |
| Final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0520, <i>wR</i> ₂ = 0.0977 | <i>R</i> ₁ = 0.0547, <i>wR</i> ₂ = 0.1475 | <i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0823 |
| Final <i>R</i> indexes [all data] | <i>R</i> ₁ = 0.0814, <i>wR</i> ₂ = 0.1056 | <i>R</i> ₁ = 0.0691, <i>wR</i> ₂ = 0.1593 | <i>R</i> ₁ = 0.0678, <i>wR</i> ₂ = 0.0919 |
| Largest diff. peak / hole / e Å ⁻³ | 2.94 / -1.69 | 2.37 / -1.77 | 1.09 / -0.58 |

Electrochemical measurements were carried out under a nitrogen atmosphere with anhydrous dichloromethane as the solvent and with tetrabutylammonium hexafluorophosphate as the electrolyte (0.20 M). The instrumentation has been described meticulously by Zanello.¹⁵ The reference electrode used for the measurements of **1** – **3** was a Ag/AgCl (3 M KCl) electrode rather than a saturated calomel electrode, which previously was used to measure the analogous PPh₃ complexes.³ The cyclic voltammograms shown below (Figures S17 – S19) are referenced to the Ag/AgCl (3 M KCl) electrode. To allow comparisons between M₃S₄ML systems with L = PPh₃ and **RuC**, the square wave voltammetry potentials are referenced to the ferrocene-ferrocenium redox couple rather than the reference electrodes, taking E^{\ominus} _{2+/3+} of ferrocene as 0.

Supporting figures

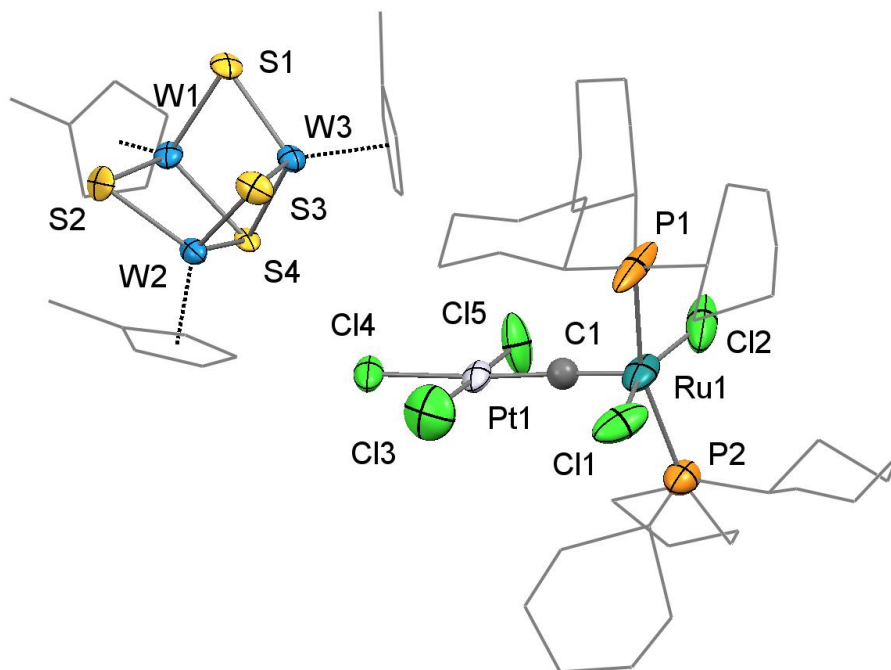


Figure S1. Representation of the decomposition product, $[(WCp')_3S_4][(Cy_3P)_2Cl_2Ru\equiv C-PtCl_3]$, which forms when **4** is left in chloroform solution for prolonged periods. Cp' and Cy of are shown as wireframe. The structure was solved partially. Unit cell data: triclinic $P\bar{1}$, $a = 11.610(2)$ Å, $b = 13.640(3)$ Å, $c = 24.753(5)$ Å, $\alpha = 95.001(6)^\circ$, $\beta = 103.462(6)^\circ$, $\gamma = 112.757(6)^\circ$, $V = 3446.1$ Å³.

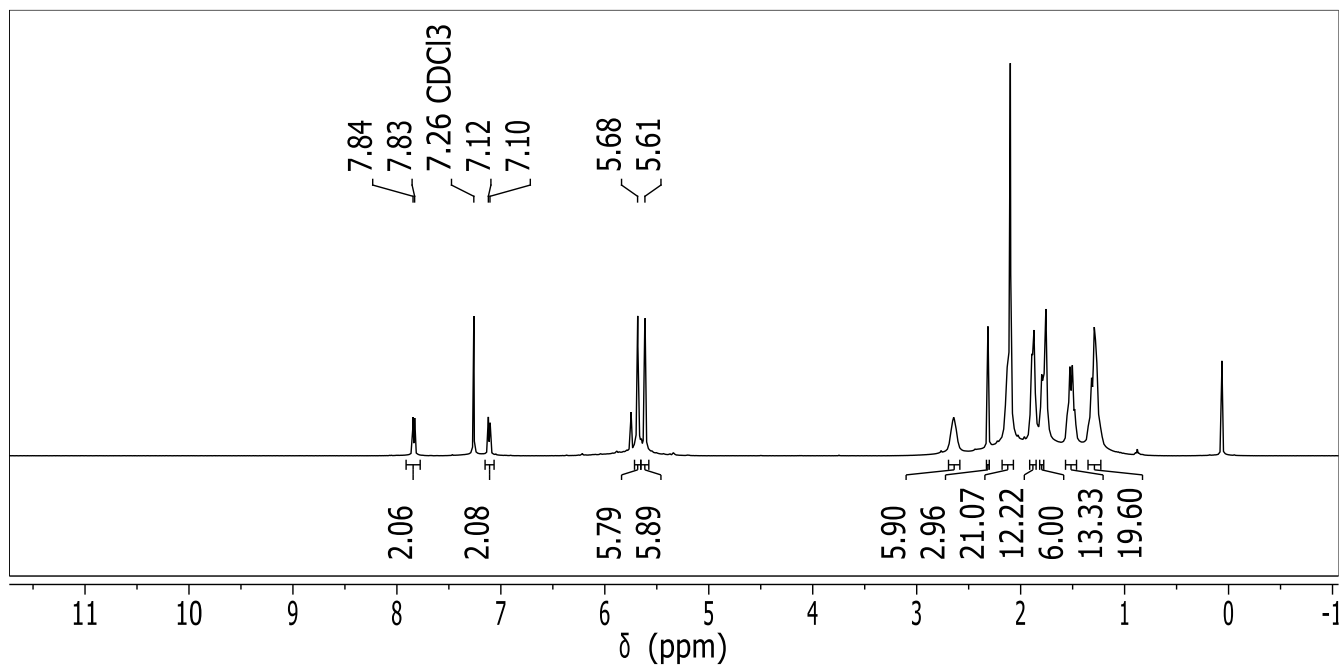


Figure S2. ¹H-NMR spectrum of **2**. The signals at 0.88 ppm and 5.75 ppm arise from traces of pentane and cyclopentadienide.

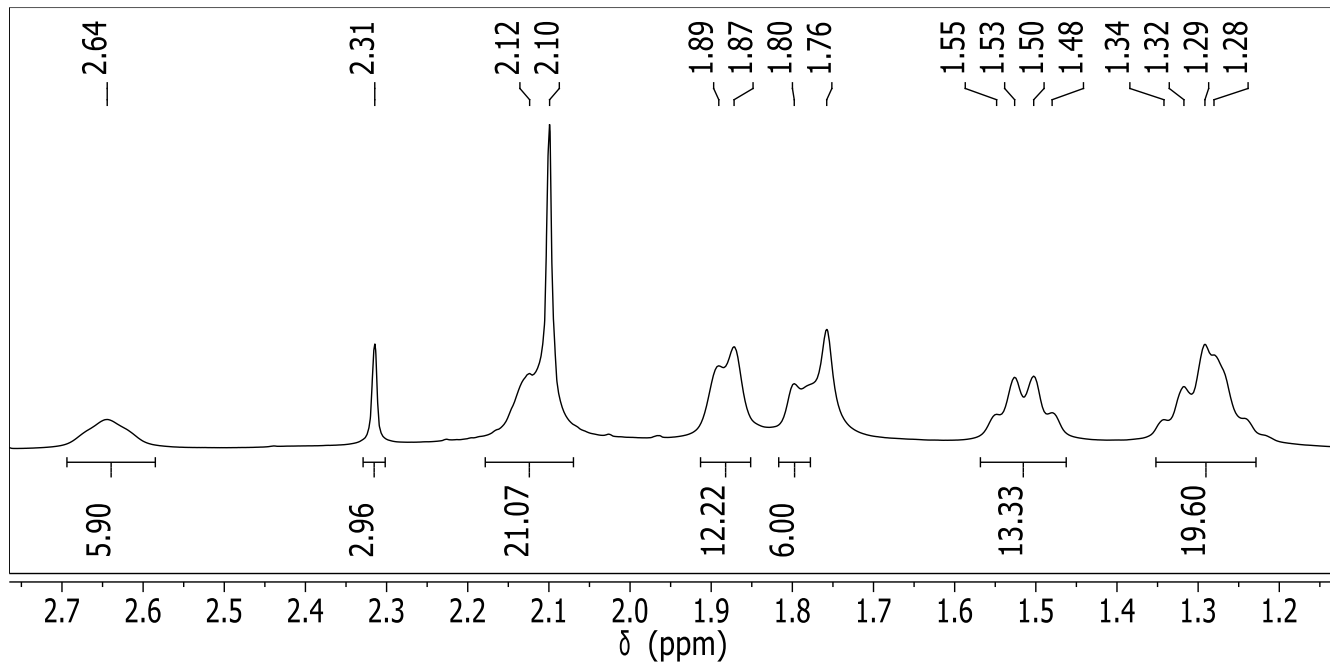


Figure S3. ¹H-NMR spectrum of **2**, magnification. The signal at 1.76 arises from a trace of water.

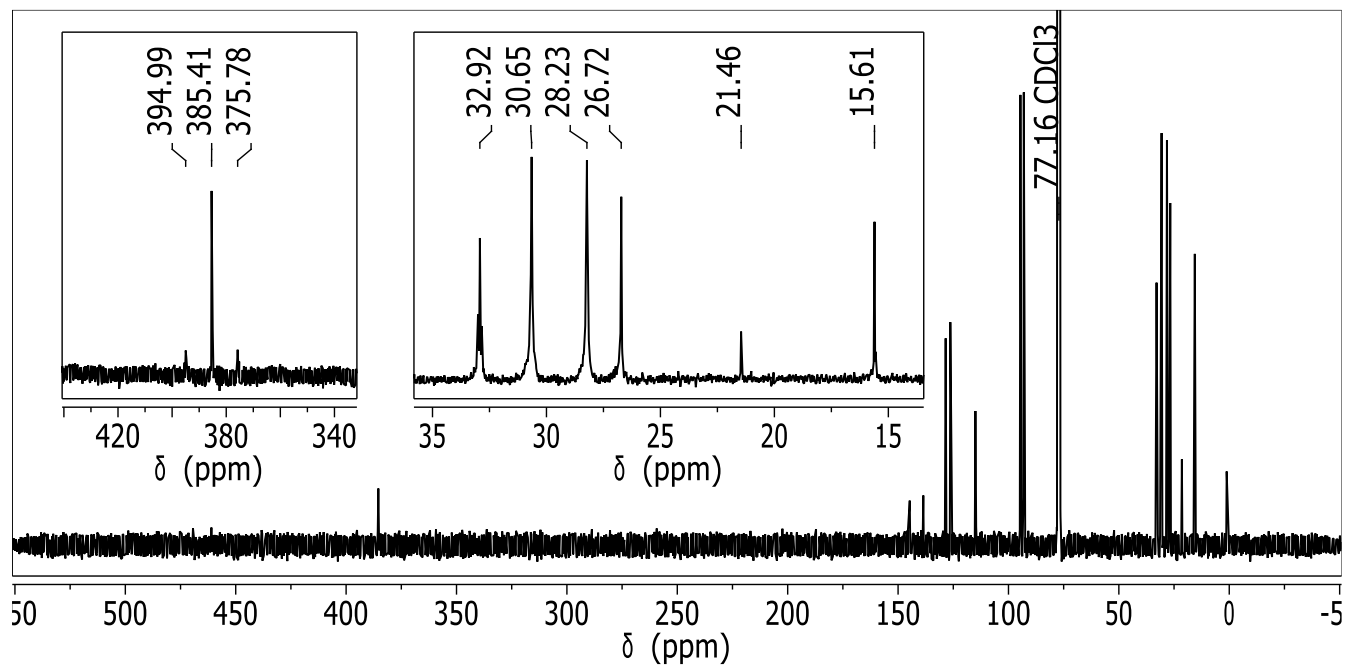


Figure S4. ^{13}C -NMR spectrum of **2**.

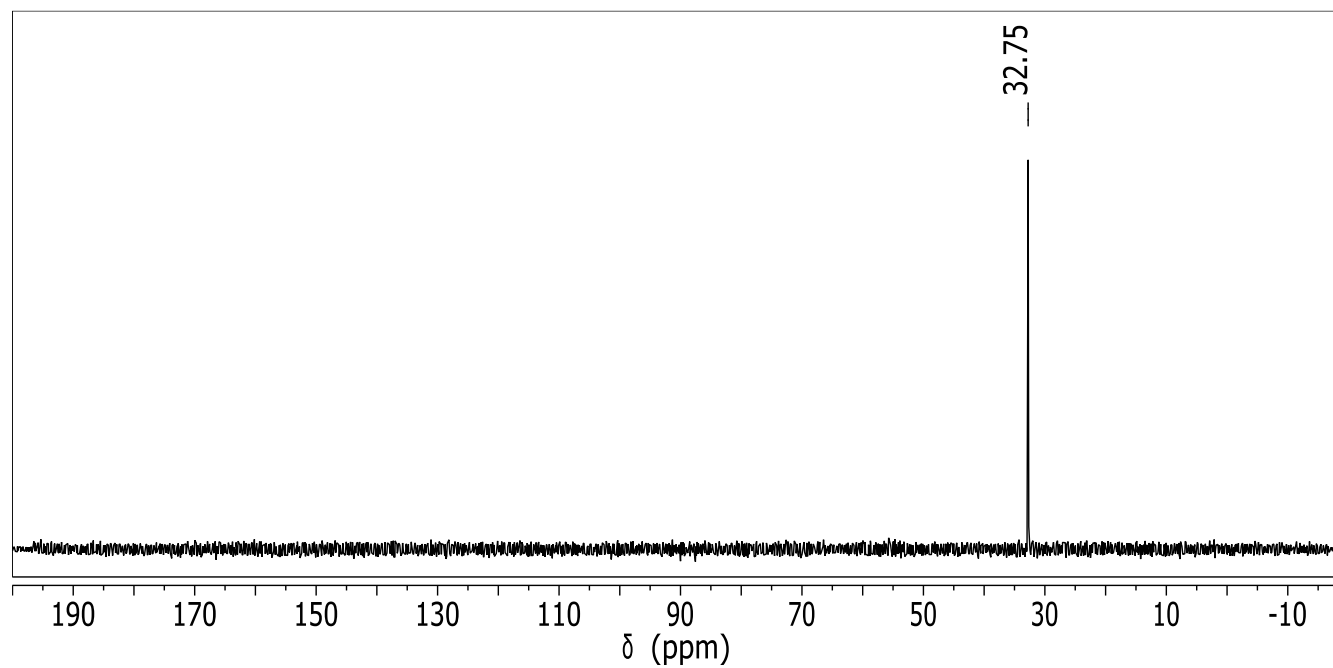


Figure S5. ^{31}P -NMR spectrum of **2**.

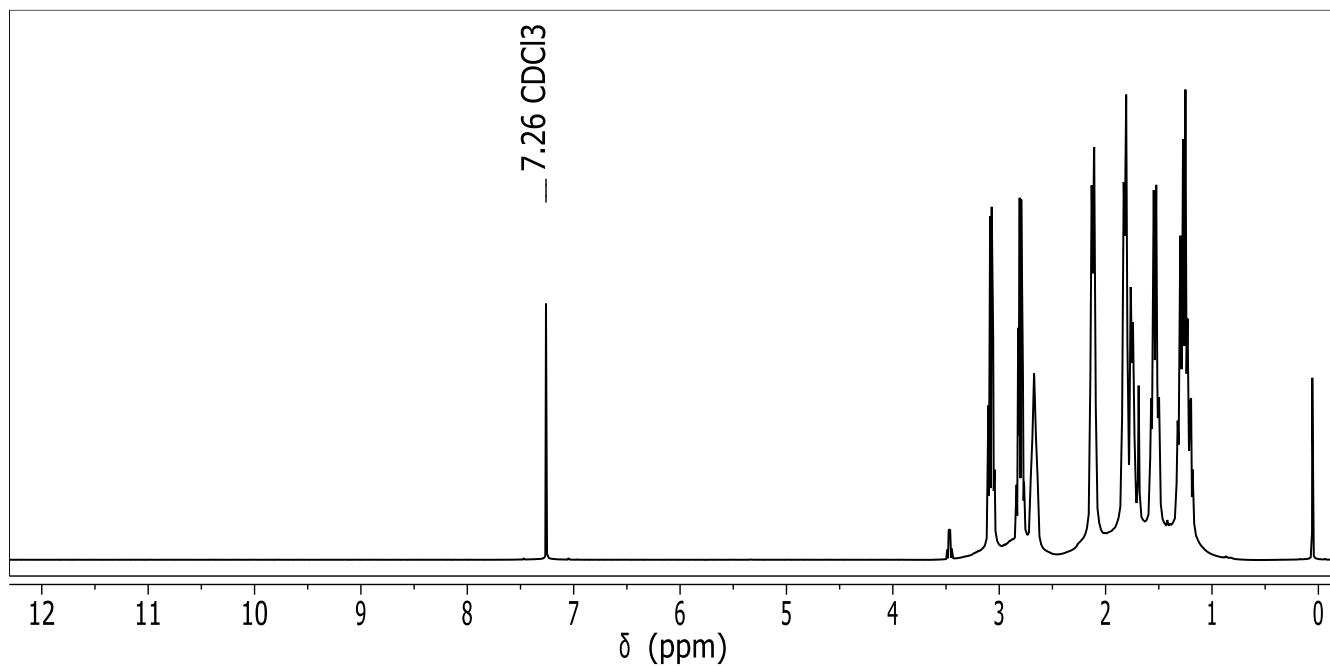


Figure S6. $^1\text{H-NMR}$ spectrum of **5**.

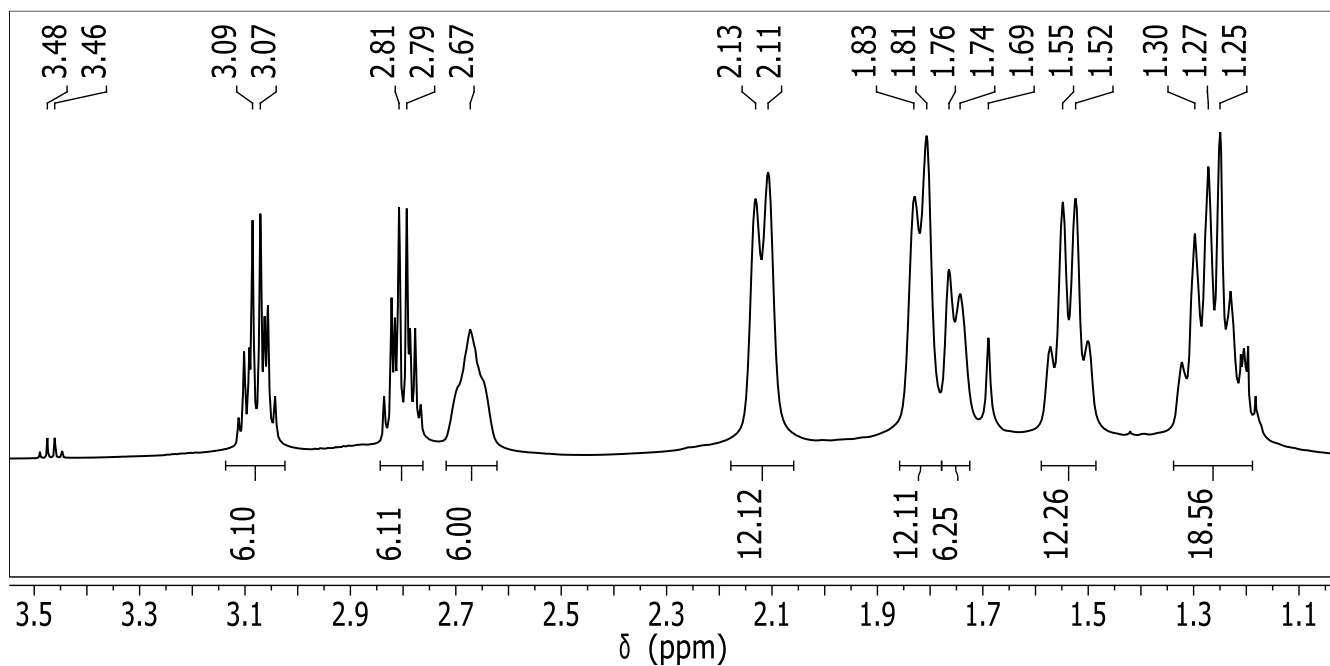


Figure S7. $^1\text{H-NMR}$ spectrum of **5**, magnification. The signals at 3.48 ppm and 1.69 arise from traces of diethyl ether and water.

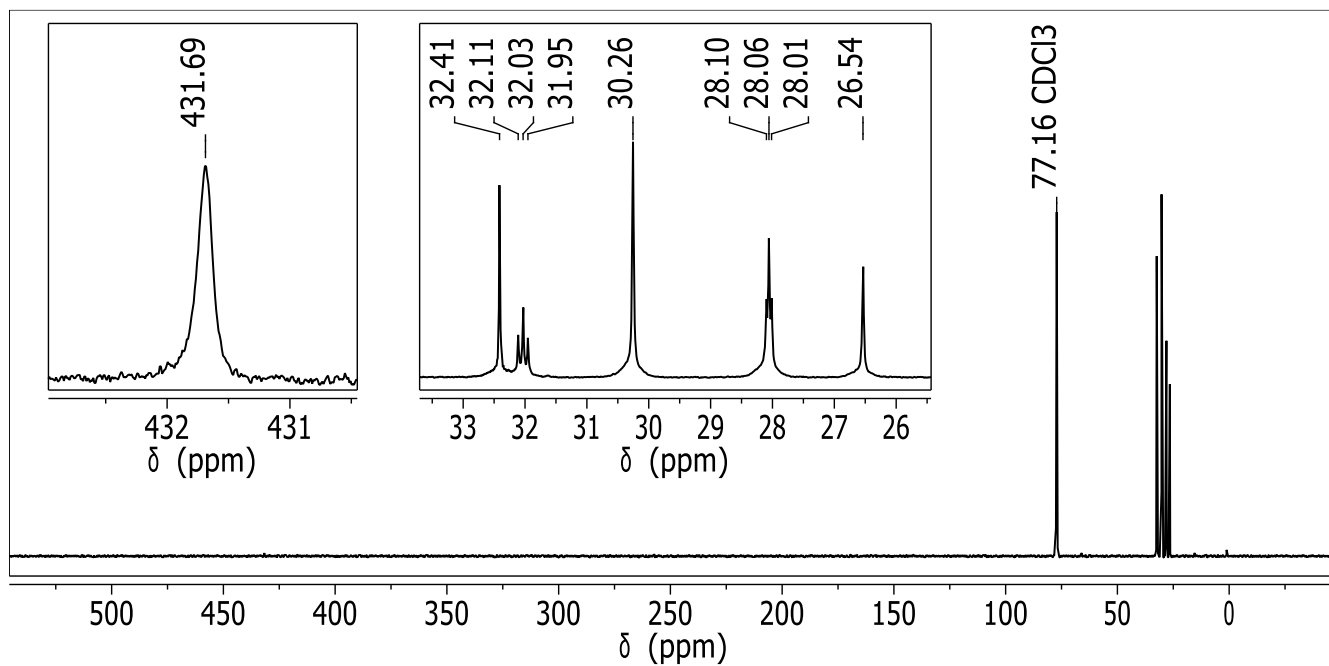


Figure S8. ^{13}C -NMR spectrum of **5**.

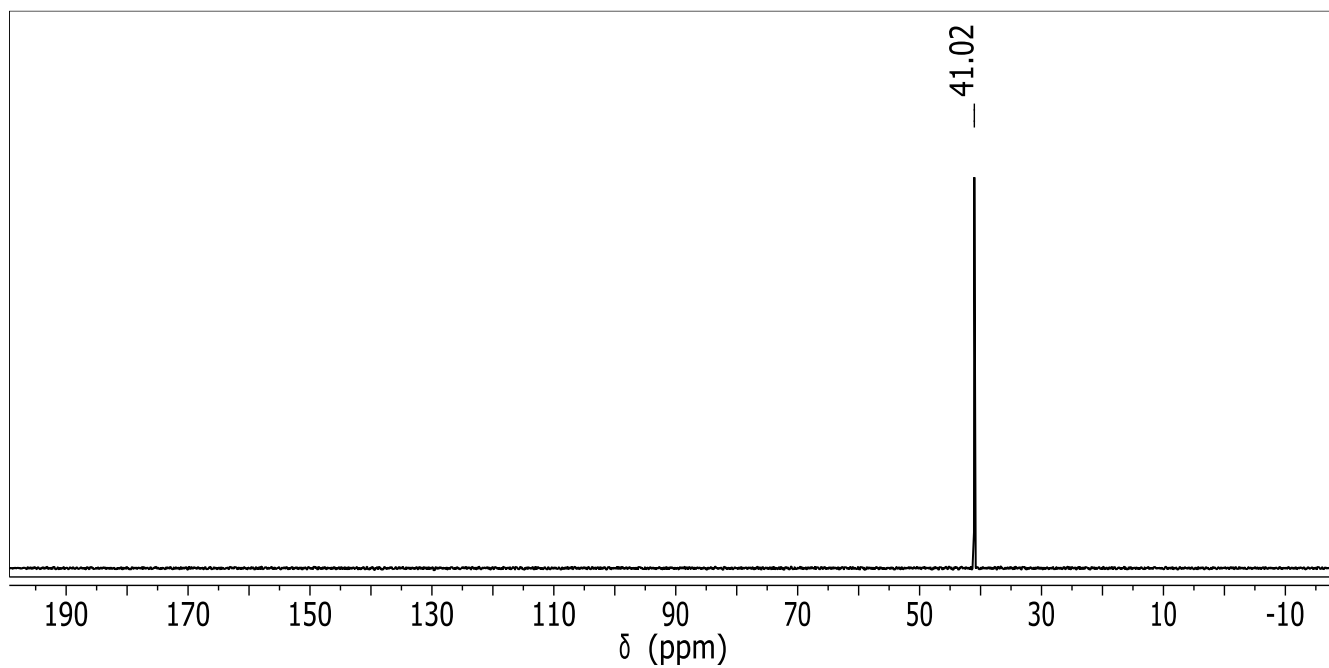


Figure S9. ^{31}P -NMR spectrum of **5**.

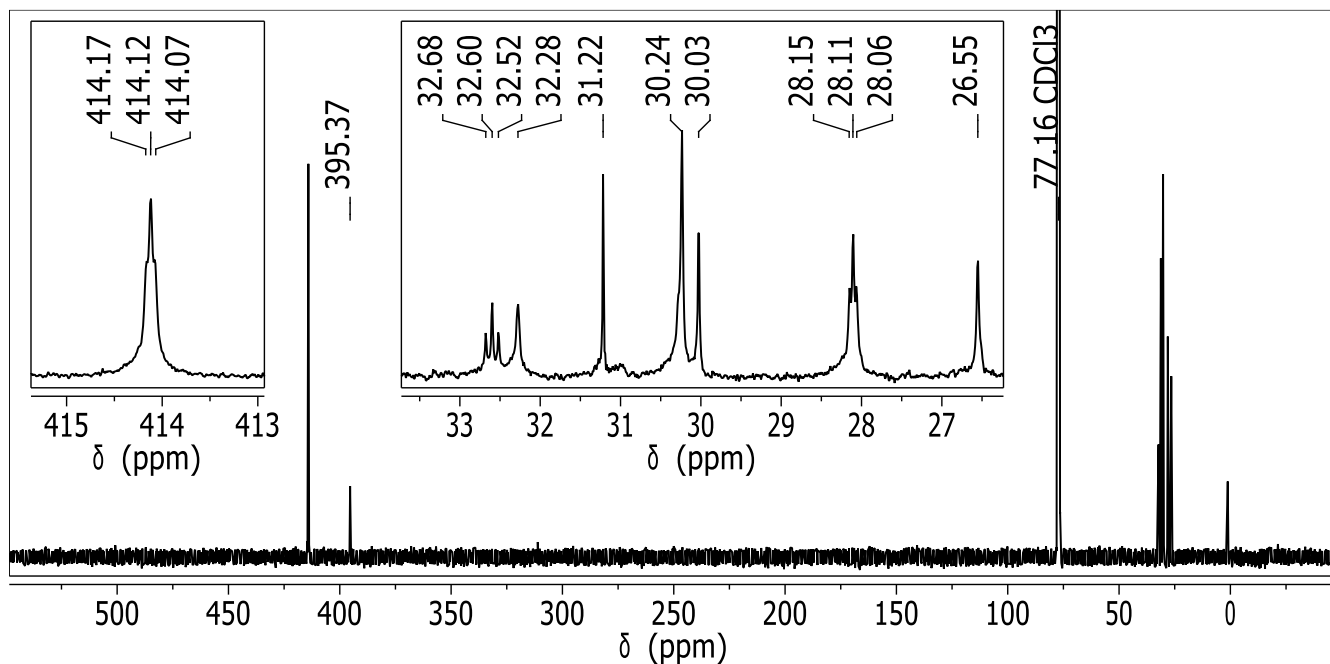


Figure S10. ^{13}C -NMR spectrum of the reaction mixture containing **7**.

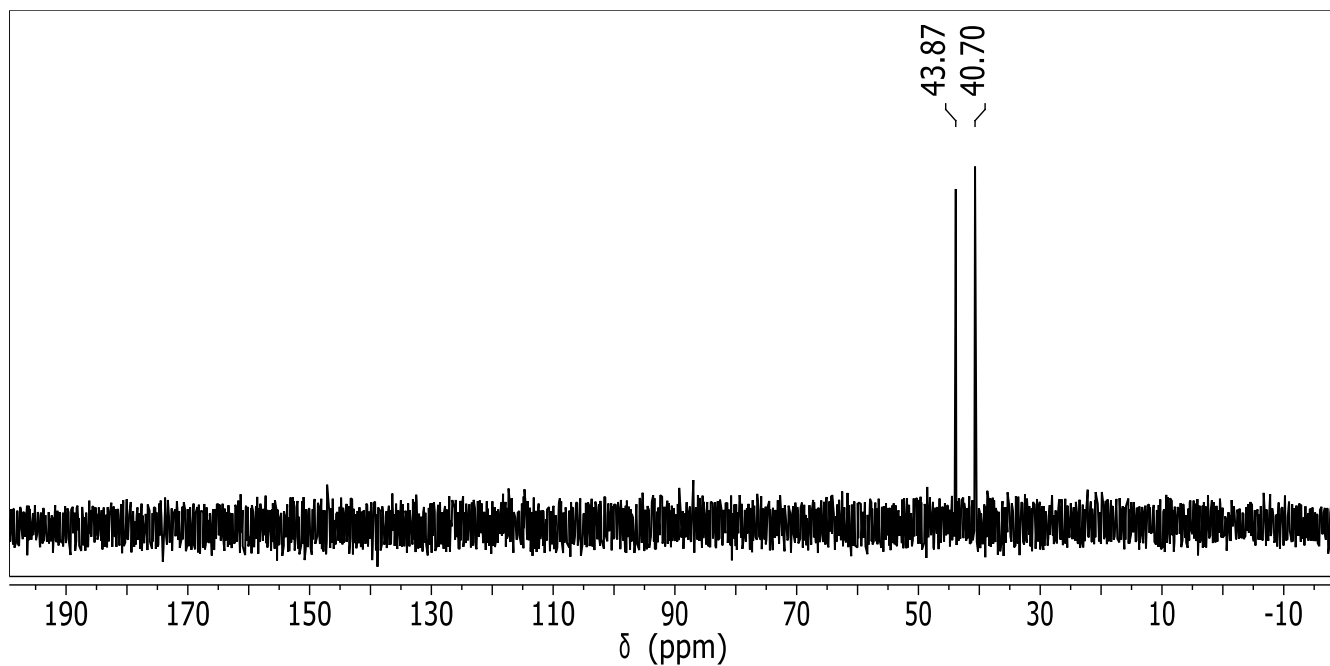


Figure S11. ^{31}P -NMR spectrum of the reaction mixture containing **7**. The resonance at 43.87 ppm arises from $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}-\text{AuCl}$ [$\delta(^{31}\text{P}) = 43.86$ ppm].⁸ $\{(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}\equiv\text{C}\}_2\text{Au}^+$ is absent [$\delta(^{31}\text{P}) = 51.11$ ppm].⁸

Generic Display Report

Analysis Info

Analysis Name D:\Data\analyser-routine\acq0878_000001.d
Method XR_ESI_pos_400_2000_4M
Sample Name RuCAu(ttcn)+
Comment

Acquisition Date 11/10/2014 9:00:56 AM

Operator
Instrument solarIX XR

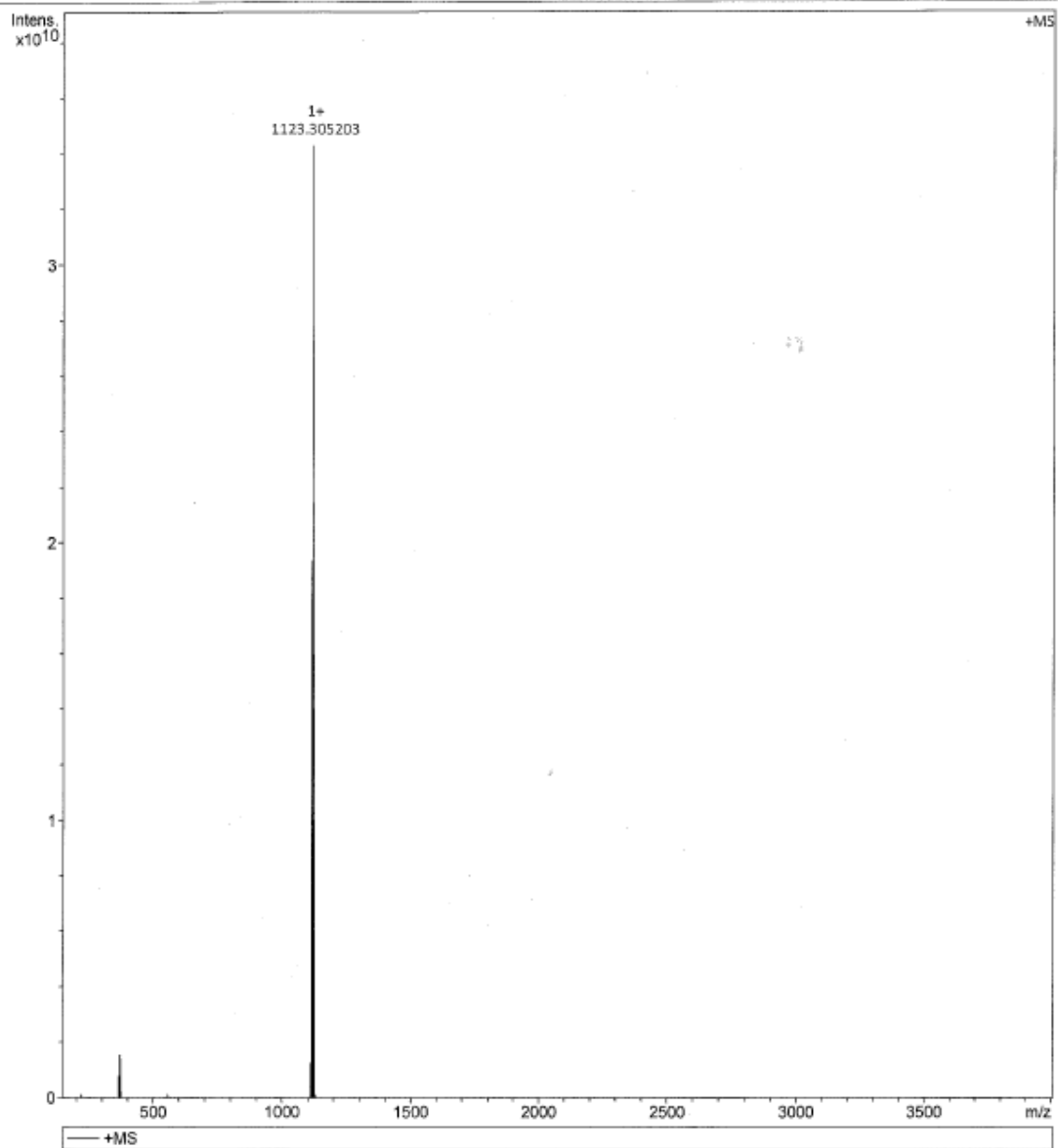


Figure S12. ESI⁺ MS spectrum of 7.

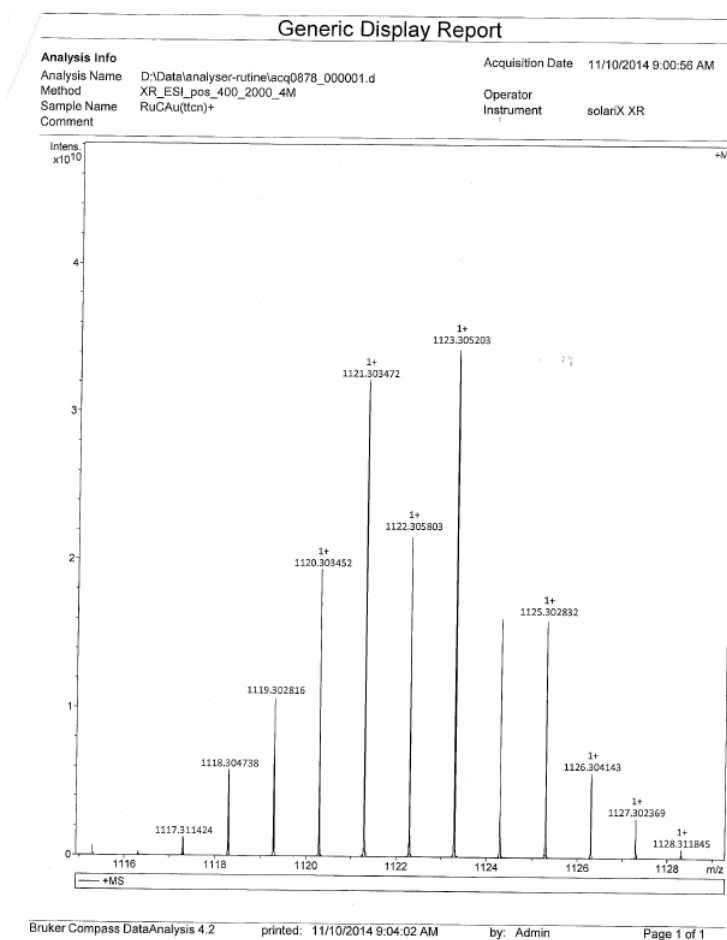


Figure S13. ESI⁺ MS spectrum of **7**.

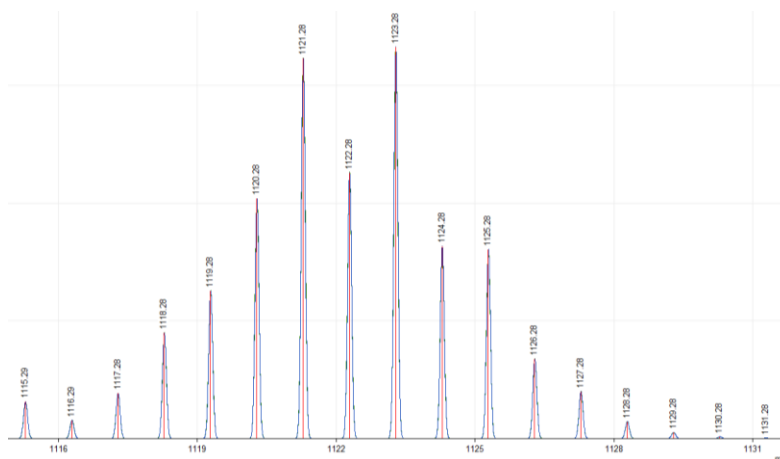


Figure S14. Simulated mass spectrum of the cation in **7**. (Using mMass: Strohm M., Kavan D., Novák P., Volný M., Havlíček V., *Anal Chem* 82 (11), 4648-4651 (2010), DOI: [10.1021/ac100818g](https://doi.org/10.1021/ac100818g))

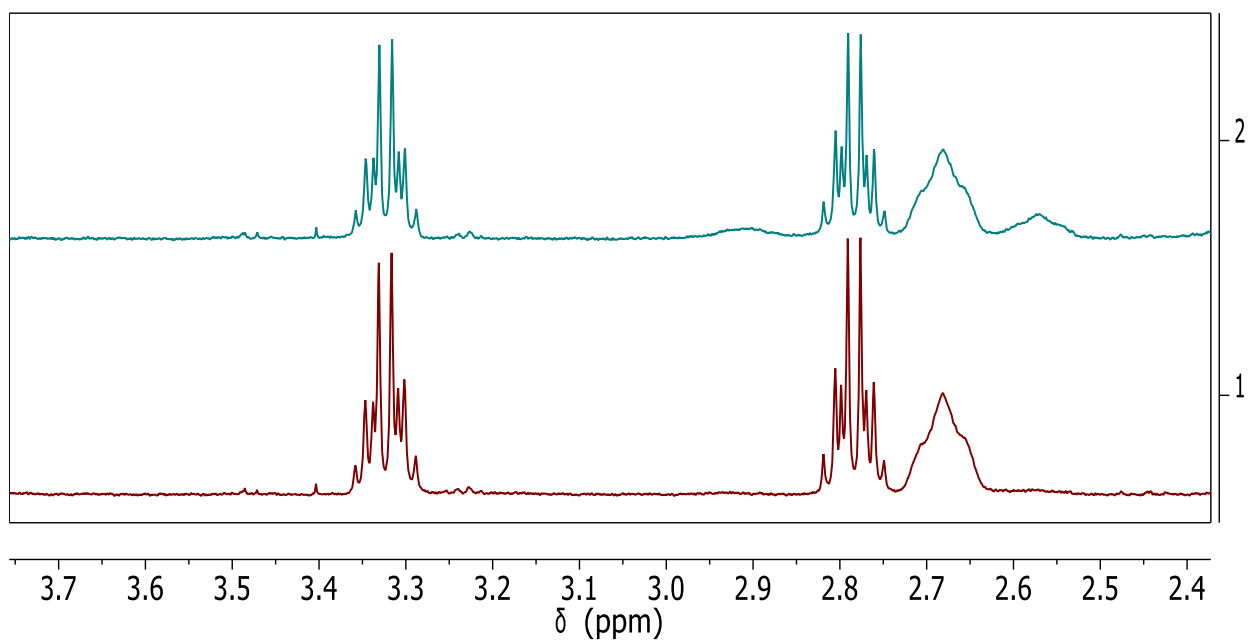


Figure S15. $^1\text{H-NMR}$: conversion of **5** (multiplet at 2.68 ppm) to **3** (multiplet at 2.57 ppm) upon reaction with $[(\text{WCp}')_3\text{S}_4\text{Pd}(\text{dba})]\text{OTs}$. Spectra 1 and 2 were recorded after 15 min and 21 h.

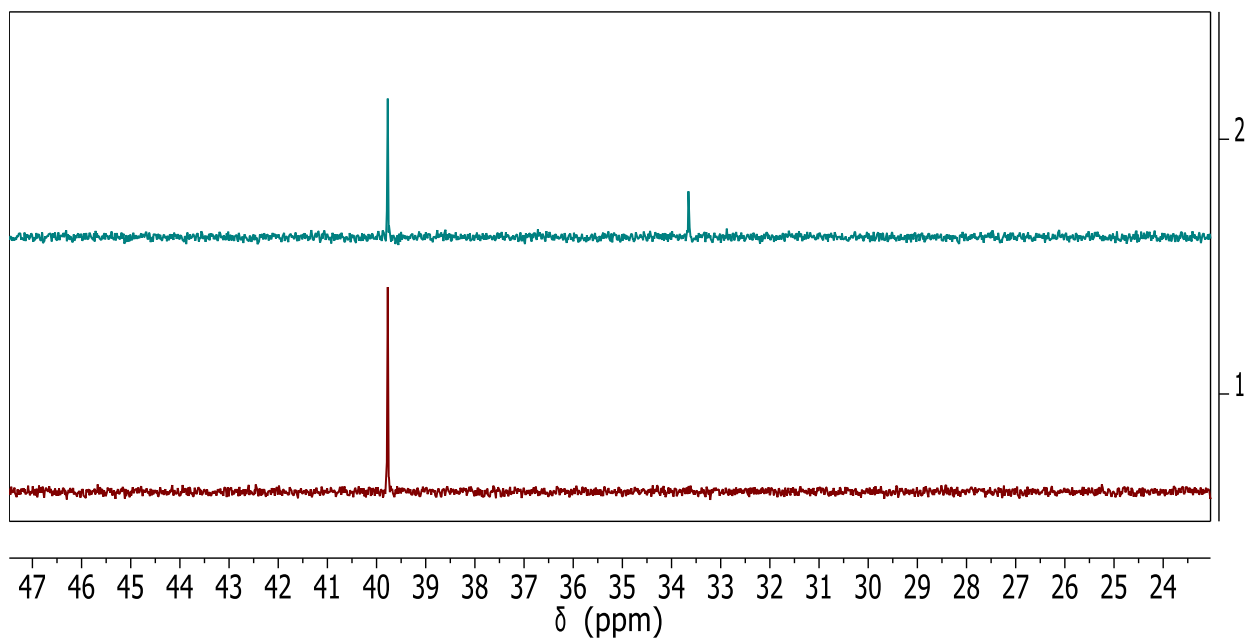


Figure S16. $^{31}\text{P-NMR}$: conversion of **5** (resonance at 39.8 ppm) to **3** (resonance at 33.7 ppm) upon reaction with $[(\text{WCp}')_3\text{S}_4\text{Pd}(\text{dba})]\text{OTs}$. Spectra 1 and 2 were recorded after 15 min and 21 h.

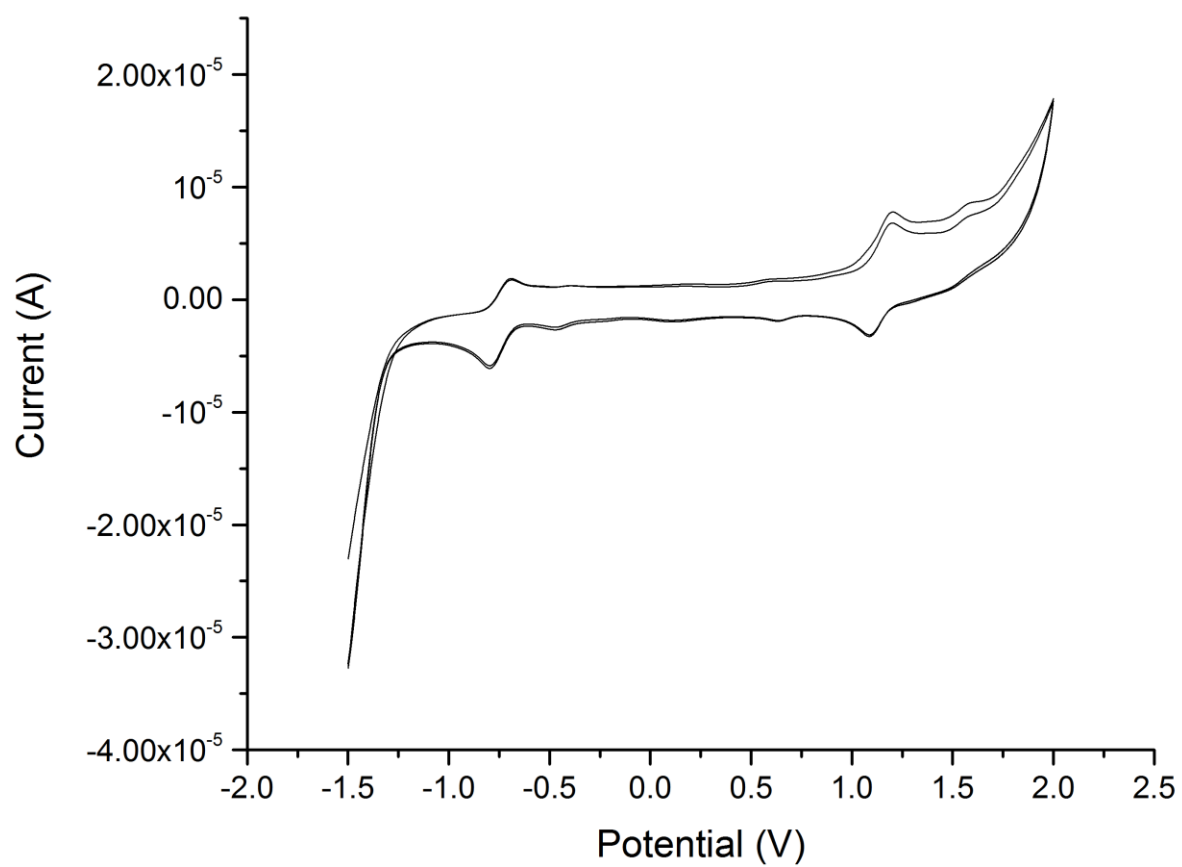


Figure S17. Cyclic voltammogram of **1**. The potentials are referenced to the Ag/AgCl (3 M KCl) electrode. Scan rate: 0.4 V s^{-1} .

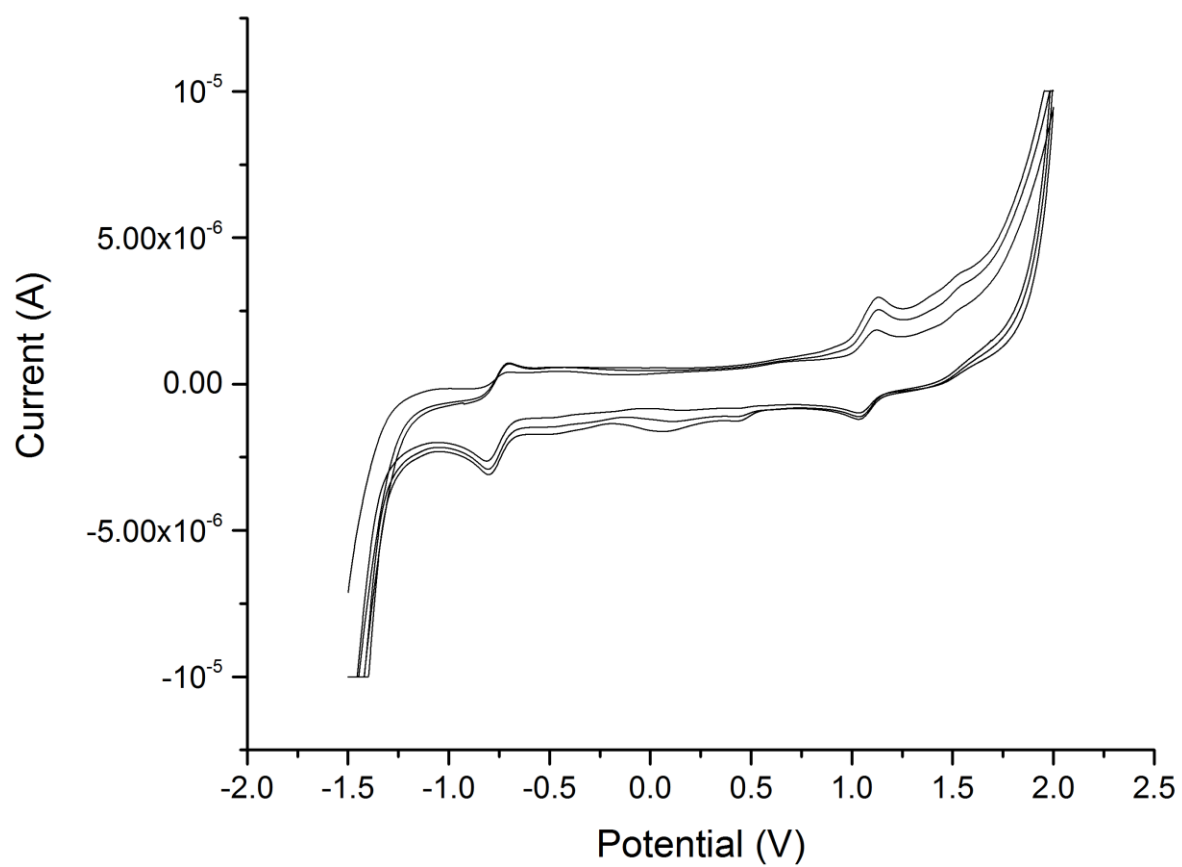


Figure S18. Cyclic voltammogram of **2**. The potentials are referenced to the Ag/AgCl (3 M KCl) electrode. Scan rate: 0.2 V s^{-1} .

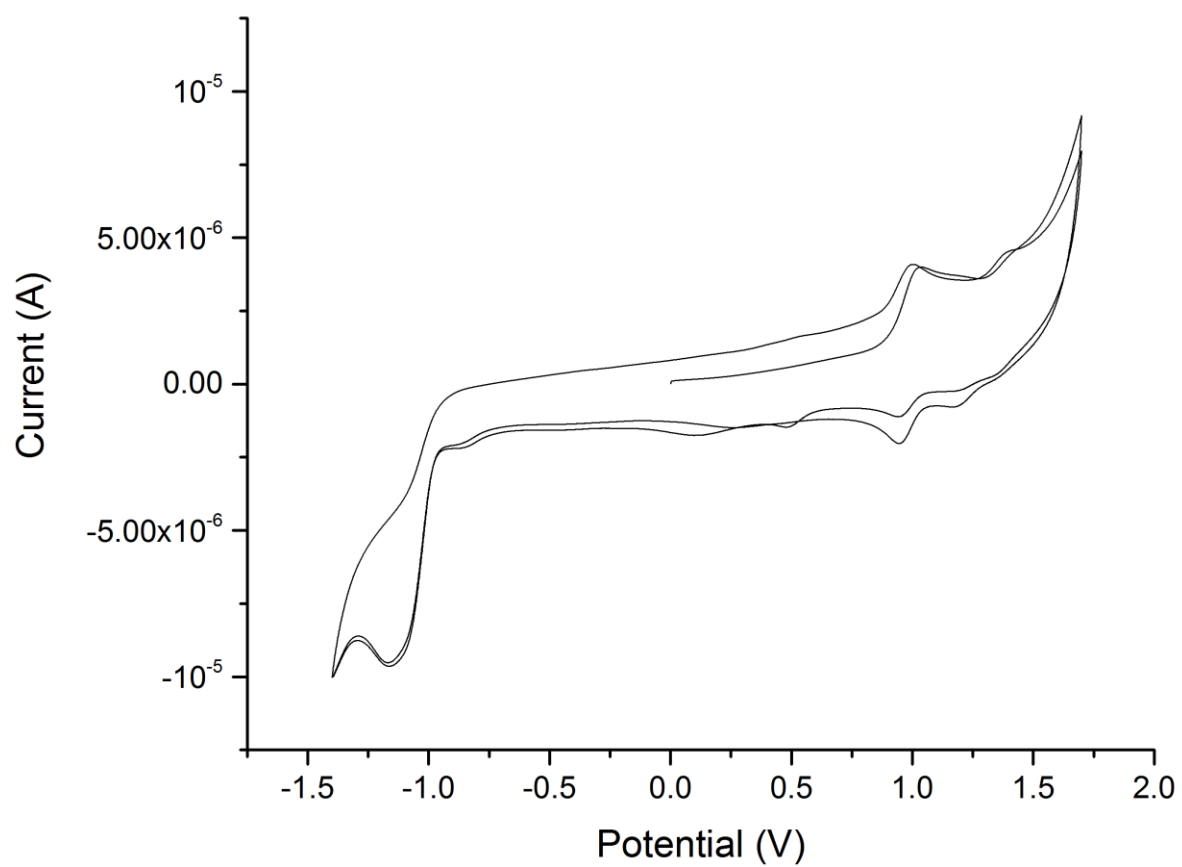


Figure S19. Cyclic voltammogram of **3**. The potentials are referenced to the Ag/AgCl (3 M KCl) electrode. Scan rate: 1.0 V s^{-1} .

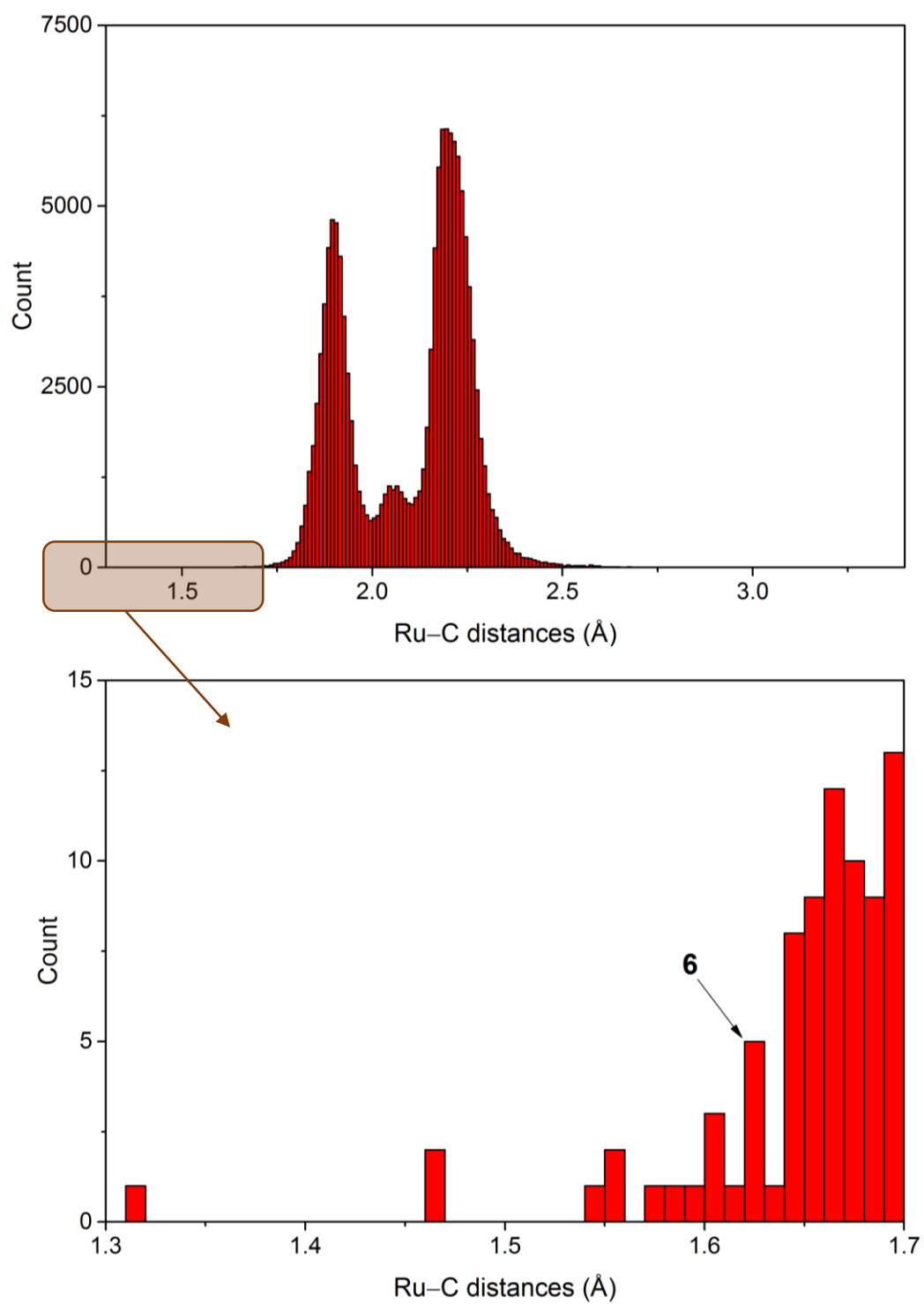


Figure S20. Histogram with Ru-C distances from the Cambridge Structural Database v. 1.17, and a zoom on the range where the Ru-C distance in **6** falls (shortest 0.01%).

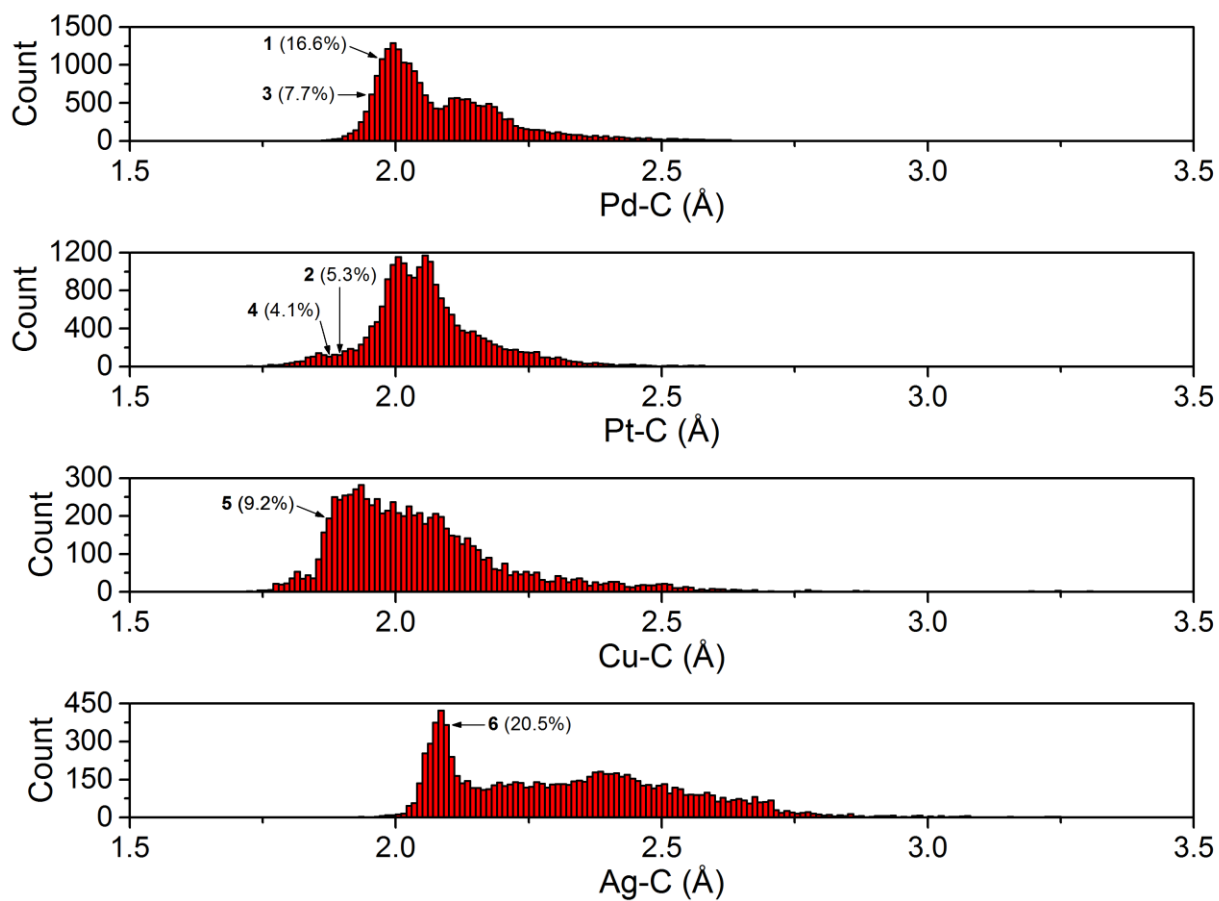


Figure S21. Histograms with M-C distances (M = Pd, Pt, Cu, and Ag) from the Cambridge Structural Database v. 1.17. **Ru**C-M distances are indicated by arrows.

References

1. S. R. Caskey, M. H. Stewart, J. E. Kivela, J. R. Sootsman, M. J. A. Johnson and J. W. Kampf, *J. Am. Chem. Soc.*, 2005, **127**, 16750-16751.
2. K. Herbst, B. Rink, L. Dahlenburg and M. Brorson, *Organometallics*, 2001, **20**, 3655-3660.
3. K. Herbst, P. Zanello, M. Corsini, N. D'Amelio, L. Dahlenburg and M. Brorson, *Inorg. Chem.*, 2003, **42**, 974-981.
4. D. Sellmann and L. Zapf, *Angew. Chem.*, 1984, **96**, 799-800.
5. G. J. Kubas, B. Monzyk and A. L. Crumbliss, in *Inorg. Synth.*, John Wiley & Sons, Inc., 1979, vol. 19, pp. 90-92.
6. P. J. Blower, J. A. Clarkson, S. C. Rawle, J. R. Hartman, R. E. Wolf, R. Yagbasan, S. G. Bott and S. R. Cooper, *Inorg. Chem.*, 1989, **28**, 4040-4046.
7. R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray and J. P. Fackler, in *Inorg. Synth.*, John Wiley & Sons, Inc., 1989, vol. 26, pp. 85-91.
8. A. Reinholdt, J. E. Vibenholt, T. J. Morsing, M. Schau-Magnussen, N. E. A. Reeler and J. Bendix, *Chem. Sci.*, 2015, **6**, 5815-5823.
9. R. Uson, J. Fornies, M. Tomas, I. Ara, J. M. Casas and A. Martin, *J. Chem. Soc., Dalton Trans.*, 1991, DOI: 10.1039/DT9910002253, 2253-2264.
10. Bruker; Bruker AXS, Inc. SAINT, Version 7.68A; Bruker AXS: Madison, WI, 2009.
11. G. Sheldrick, SADABS, Version 2008/2; University of Göttingen: Germany, 2003.
12. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
13. L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Crystallogr., Sect. A*, 2015, **71**, 59-75.
14. G. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.
15. P. Zanello, F. Laschi, M. Fontani, C. Mealli, A. Ienco, K. Tang, X. Jin and L. Li, *J. Chem. Soc., Dalton Trans.*, 1999, DOI: 10.1039/A807500J, 965-970.