Supporting Information

An Anionic Dinuclear Ruthenium Dihydrogen Complex of Relevance for Alkyne gem-Hydrogenation

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Supporting Crystallographic Data

Figure S1. The molecular structure of complex 8·(pentane) in the solid state; H-atoms were removed for clarity.

X-ray Crystal Structure Analysis of Complex 8·(pentane): C_{39}H_{57}ClN_{2}Ru, M_r = 690.38 g mol⁻¹, yellow plate, crystal size 0.100 x 0.048 x 0.042 mm³, monoclinic, space group P2₁/n [14], a = 13.1675(9) Å, b = 12.1818(8) Å, c = 22.5540(15) Å, β = 100.054(3)°, V = 3562.2(4) Å³, T = 100(2) K, Z = 4, D_\text{calc} = 1.287 g·cm⁻³, λ = 0.71073 Å, μ(Mo-Kα) = 0.544 mm⁻¹, Gaussian absorption correction (T_{\text{min}} = 0.96165, T_{\text{max}} = 0.98642), Bruker-AXS Kappa Mach3 with APEX-II detector and IμS microfocus source, 1.675 < θ < 31.744°, 117341 measured reflections, 11966 independent reflections, 10447 reflections with I > 2σ(I), R_\text{int} = 0.0357. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against F² to R₁ = 0.0330 [I > 2σ(I)], wR₂ = 0.0708, 403 parameters, 0 restraints. CCDC-2143698
**Figure S2.** Crystal faces and unit cell determination/refinement of 8-pentane

**INTENSITY STATISTICS FOR DATASET**

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean | I | Mean I/s | Rmerge | Rsigma |
|------------|------|---------|-----------|------------|------|---|----------|--------|--------|
| Inf - 2.88 | 187  | 187     | 100.0     | 15.40      | 94.37| 111.67| 0.0177   | 0.0070 |
| 2.88 - 1.88| 441  | 441     | 100.0     | 16.95      | 52.38| 100.13| 0.0192   | 0.0072 |
| 1.88 - 1.29| 630  | 630     | 100.0     | 17.11      | 37.22| 86.94 | 0.0213   | 0.0080 |
| 1.48 - 1.72| 627  | 627     | 100.0     | 17.17      | 22.71| 71.45 | 0.0271   | 0.0097 |
| 1.29 - 1.17| 616  | 616     | 100.0     | 16.72      | 19.39| 64.29 | 0.0329   | 0.0111 |
| 1.17 - 1.08| 665  | 665     | 100.0     | 15.17      | 16.67| 54.70 | 0.0378   | 0.0132 |
| 1.08 - 1.01| 684  | 684     | 100.0     | 11.65      | 16.83| 45.10 | 0.0383   | 0.0160 |
| 1.01 - 0.96| 633  | 633     | 100.0     | 9.95       | 14.66| 36.86 | 0.0435   | 0.0195 |
| 0.96 - 0.92| 595  | 595     | 100.0     | 8.71       | 10.52| 27.92 | 0.0546   | 0.0264 |
| 0.92 - 0.88| 694  | 694     | 100.0     | 7.91       | 10.17| 25.69 | 0.0566   | 0.0289 |
| 0.88 - 0.85| 632  | 632     | 100.0     | 7.56       | 8.80 | 22.94 | 0.0631   | 0.0339 |
| 0.85 - 0.83| 461  | 461     | 100.0     | 7.32       | 7.98 | 20.87 | 0.0684   | 0.0377 |
| 0.83 - 0.80| 792  | 792     | 100.0     | 7.08       | 7.40 | 18.30 | 0.0756   | 0.0417 |
| 0.80 - 0.78| 574  | 574     | 100.0     | 6.79       | 6.92 | 17.02 | 0.0822   | 0.0465 |
| 0.78 - 0.76| 679  | 679     | 100.0     | 6.59       | 6.71 | 16.01 | 0.0871   | 0.0498 |
| 0.76 - 0.74| 737  | 737     | 100.0     | 6.49       | 6.35 | 14.71 | 0.0926   | 0.0545 |
| 0.74 - 0.73| 374  | 374     | 100.0     | 6.22       | 6.63 | 14.75 | 0.0961   | 0.0548 |
| 0.73 - 0.71| 863  | 863     | 100.0     | 6.14       | 5.72 | 12.78 | 0.1056   | 0.0639 |
| 0.71 - 0.70| 482  | 482     | 100.0     | 5.87       | 5.41 | 11.81 | 0.1092   | 0.0705 |
| 0.70 - 0.68| 1110 | 1244    | 89.2      | 4.40       | 5.10 | 9.90  | 0.1198   | 0.0890 |
| 0.78 - 0.68| 4245 | 4379    | 96.9      | 5.75       | 5.87 | 12.94 | 0.1013   | 0.0650 |
| Inf - 0.68 | 12476| 12610   | 98.9      | 9.52       | 14.39| 34.67 | 0.0353   | 0.0223 |
Table S1. Crystal Data and Structure Refinement.

| Parameter                          | Value                                      |
|------------------------------------|--------------------------------------------|
| Identification code                | 8·(pentane) (internal: 13101)              |
| Empirical formula                  | C_{39}H_{57}ClN_{2}Ru                      |
| Color                              | yellow                                     |
| Formula weight                     | 690.38 g·mol⁻¹                             |
| Temperature                        | 100(2) K                                   |
| Wavelength                         | 0.71073 Å                                  |
| Crystal system                     | MONOCLINIC                                 |
| Space group                        | P2₁/n, (no. 14)                            |
| Unit cell dimensions               | a = 13.1675(9) Å, α = 90°                 |
|                                    | b = 12.1818(8) Å, β = 100.054(3)°         |
|                                    | c = 22.5540(15) Å, γ = 90°                |
| Volume                             | 3562.2(4) Å³                              |
| Z                                  | 4                                          |
| Density (calculated)               | 1.287 Mg · m⁻³                             |
| Absorption coefficient             | 0.544 mm⁻¹                                 |
| F(000)                             | 1464 e                                     |
| Crystal size                       | 0.100 x 0.048 x 0.042 mm³                  |
| θ range for data collection        | 1.675 to 31.744°.                         |
| Index ranges                       | -19 ≤ h ≤ 19, -17 ≤ k ≤ 17, -33 ≤ l ≤ 32 |
| Reflections collected              | 117341                                     |
| Independent reflections            | 11966 [R_{int} = 0.0357]                   |
| Reflections with I>2σ(I)           | 10447                                      |
| Completeness to θ = 25.242°        | 100.0 %                                    |
| Absorption correction              | Gaussian                                   |
| Max. and min. transmission         | 0.99 and 0.96                             |
| Refinement method                  | Full-matrix least-squares on F²            |
| Data / restraints / parameters      | 11966 / 0 / 403                            |
| Goodness-of-fit on F²              | 1.119                                      |
| Final R indices [I>2σ(I)]          | R₁ = 0.0330, wR² = 0.0708                 |
| R indices (all data)               | R₁ = 0.0415, wR² = 0.0736                 |
| Largest diff. peak and hole        | 0.8 and -0.7 e · Å⁻³                       |
Table S2. Complex 8-(pentane): Bond lengths [Å] and Angles ['].

| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| Ru(1)-H               | 1.51(2)    | Ru(1)-Cl(1)           | 2.4018(4)  |
| Ru(1)-C(1)            | 2.0483(13) | Ru(1)-C(28)           | 2.2809(16) |
| Ru(1)-C(29)           | 2.3191(15) | Ru(1)-C(30)           | 2.2168(16) |
| Ru(1)-C(31)           | 2.1829(17) | Ru(1)-C(32)           | 2.1789(17) |
| Ru(1)-C(33)           | 2.2417(16) | N(1)-C(1)             | 1.3730(17) |
| N(1)-C(2)             | 1.3916(17) | N(1)-C(4)             | 1.4433(18) |
| N(2)-C(1)             | 1.3731(17) | N(2)-C(3)             | 1.3900(18) |
| N(2)-C(16)            | 1.4407(18) | C(2)-H(2)             | 0.9500     |
| C(2)-C(3)             | 1.343(2)   | C(3)-H(3)             | 0.9500     |
| C(4)-C(5)             | 1.410(2)   | C(4)-C(9)             | 1.398(2)   |
| C(5)-C(6)             | 1.393(2)   | C(5)-C(10)            | 1.519(2)   |
| C(6)-H(6)             | 0.9500     | C(6)-C(7)             | 1.391(2)   |
| C(7)-H(7)             | 0.9500     | C(7)-C(8)             | 1.379(2)   |
| C(8)-H(8)             | 0.9500     | C(8)-C(9)             | 1.402(2)   |
| C(9)-C(13)            | 1.517(2)   | C(10)-H(10)           | 1.0000     |
| C(10)-C(11)           | 1.528(2)   | C(10)-C(12)           | 1.535(2)   |
| C(11)-H(11A)          | 0.9800     | C(11)-H(11B)          | 0.9800     |
| C(11)-H(11C)          | 0.9800     | C(12)-H(12A)          | 0.9800     |
| C(12)-H(12B)          | 0.9800     | C(12)-H(12C)          | 0.9800     |
| C(13)-H(13)           | 1.0000     | C(13)-C(14)           | 1.535(2)   |
| C(13)-C(15)           | 1.538(2)   | C(14)-H(14A)          | 0.9800     |
| C(14)-H(14B)          | 0.9800     | C(14)-H(14C)          | 0.9800     |
| C(15)-H(15A)          | 0.9800     | C(15)-H(15B)          | 0.9800     |
| C(15)-H(15C)          | 0.9800     | C(16)-C(17)           | 1.396(2)   |
| C(16)-C(21)           | 1.407(2)   | C(17)-C(18)           | 1.402(2)   |
| C(17)-C(22)           | 1.521(2)   | C(18)-H(18)           | 0.9500     |
| C(18)-C(19)           | 1.380(2)   | C(19)-H(19)           | 0.9500     |
| C(19)-C(20)           | 1.390(2)   | C(20)-H(20)           | 0.9500     |
| C(20)-C(21)           | 1.398(2)   | C(21)-C(25)           | 1.520(2)   |
| C(22)-H(22)           | 1.0000     | C(22)-C(23)           | 1.527(2)   |
| C(22)-C(24)           | 1.531(2)   | C(23)-H(23A)          | 0.9800     |
| C(23)-H(23B)          | 0.9800     | C(23)-H(23C)          | 0.9800     |
| Bond                  | Distance | Bond                  | Distance |
|-----------------------|----------|-----------------------|----------|
| C(24)-H(24A)          | 0.9800   | C(24)-H(24B)          | 0.9800   |
| C(24)-H(24C)          | 0.9800   | C(25)-H(25)           | 1.0000   |
| C(25)-C(26)           | 1.531(2) | C(25)-C(27)           | 1.531(2) |
| C(26)-H(26A)          | 0.9800   | C(26)-H(26B)          | 0.9800   |
| C(26)-H(26C)          | 0.9800   | C(27)-H(27A)          | 0.9800   |
| C(27)-H(27B)          | 0.9800   | C(27)-H(27C)          | 0.9800   |
| C(28)-C(29)           | 1.406(2) | C(28)-C(33)           | 1.410(3) |
| C(29)-C(30)           | 1.401(3) | C(30)-H(30)           | 0.9500   |
| C(30)-C(31)           | 1.413(3) | C(31)-H(31)           | 0.9500   |
| C(31)-C(32)           | 1.424(3) | C(32)-H(32)           | 0.9500   |
| C(32)-C(33)           | 1.397(3) | C(33)-H(33)           | 0.9500   |
| C(34)-H(34A)          | 0.9800   | C(34)-H(34B)          | 0.9800   |
| C(34)-H(34C)          | 0.9800   | C(91)-H(91A)          | 0.9800   |
| C(91)-H(91B)          | 0.9800   | C(91)-H(91C)          | 0.9800   |
| C(91)-C(92)           | 1.508(3) | C(92)-H(92A)          | 0.9900   |
| C(92)-H(92B)          | 0.9900   | C(92)-C(93)           | 1.528(3) |
| C(93)-H(93A)          | 0.9900   | C(93)-H(93B)          | 0.9900   |
| C(93)-C(94)           | 1.530(3) | C(94)-H(94A)          | 0.9900   |
| C(94)-H(94B)          | 0.9900   | C(94)-C(95)           | 1.528(3) |
| C(95)-H(95A)          | 0.9800   | C(95)-H(95B)          | 0.9800   |
| C(95)-H(95C)          | 0.9800   |                       |          |
| Cl(1)-Ru(1)-H         | 84.6(9)  | C(1)-Ru(1)-H          | 77.7(8)  |
| Cl(1)-Ru(1)-Cl(1)     | 84.81(4) | C(1)-Ru(1)-C(28)      | 146.12(6) |
| Cl(1)-Ru(1)-C(29)     | 115.51(6) | C(1)-Ru(1)-C(30)     | 99.52(6)  |
| Cl(1)-Ru(1)-C(31)     | 108.19(7) | C(1)-Ru(1)-C(32)     | 138.27(8) |
| Cl(1)-Ru(1)-C(33)     | 175.00(7) | C(28)-Ru(1)-H        | 135.0(8)  |
| C(28)-Ru(1)-Cl(1)     | 89.45(5)  | C(28)-Ru(1)-C(29)    | 35.58(6)  |
| C(29)-Ru(1)-H         | 162.7(8)  | C(29)-Ru(1)-Cl(1)    | 106.91(5) |
| C(30)-Ru(1)-H         | 135.0(9)  | C(30)-Ru(1)-Cl(1)    | 140.29(5) |
| C(30)-Ru(1)-C(28)     | 65.11(6)  | C(30)-Ru(1)-C(29)    | 35.90(7)  |
| C(30)-Ru(1)-C(33)     | 77.80(6)  | C(31)-Ru(1)-H        | 100.0(8)  |
| C(31)-Ru(1)-Cl(1)     | 166.83(5) | C(31)-Ru(1)-C(28)    | 78.55(7)  |
| C(31)-Ru(1)-C(29)     | 66.03(7)  | C(31)-Ru(1)-C(30)    | 37.46(7)  |
| C(31)-Ru(1)-C(33)     | 67.11(7)  | C(32)-Ru(1)-H        | 85.0(8)   |
Figure S3. The molecular structure of complex 9·5(CH₂Cl₂); H-atoms removed for clarity.

X-ray Crystal Structure Analysis of complex 9·5(CH₂Cl₂): C₈₆H₁₂₁Cl₁₅N₆Ru₂, Mᵣ = 1972.77 g mol⁻¹, orange prism, crystal size 0.037 x 0.032 x 0.011 mm³, monoclinic, space group C2/c [15], a = 22.8887(10) Å, b = 15.1400(6) Å, c = 27.8398(12) Å, β = 94.106(2)°, V = 9622.7(7) Å³, T = 100(2) K, Z = 4, Dₘ calc = 1.362 g·cm⁻³, λ = 0.71073 Å, μ(Mo-Kα) = 0.775 mm⁻¹, Gaussian absorption correction (Tₘᵢₙ = 0.97086, Tₘₐₓ = 0.99056), Bruker-AXS Kappa Mach3 with APEX-II detector and IµS microfocus source, 1.467 < θ < 28.280°, 139529 measured reflections, 11946 independent reflections, 10004 reflections with I > 2σ(I), Rᵣınt = 0.0543. The structure was solved by SHELXT and refined by full-matrix least-squares (SHELXL) against F² to R₁ = 0.0474 [I > 2σ(I)], wR₂ = 0.1126, 559 parameters, 10 restraints. CCDC-2143699
Figure S4. Crystal faces and unit cell determination/refinement of complex 9·5(CH₂Cl₂).

INTENSITY STATISTICS FOR DATASET

| Resolution | #Data | #Theory | %Complete | Redundancy | Mean I | Mean I/s | Rmerge | Rsigma |
|------------|-------|---------|-----------|------------|--------|----------|--------|--------|
| Inf        | 251   | 251     | 100.0     | 16.79      | 65.57  | 77.11    | 0.0240 | 0.0096 |
| 2.83       | 589   | 589     | 100.0     | 18.01      | 35.97  | 67.89    | 0.0289 | 0.0102 |
| 1.87       | 834   | 834     | 100.0     | 18.22      | 23.22  | 56.73    | 0.0356 | 0.0121 |
| 1.48       | 834   | 834     | 100.0     | 18.16      | 15.15  | 45.00    | 0.0458 | 0.0150 |
| 1.29       | 904   | 904     | 100.0     | 17.55      | 12.53  | 38.50    | 0.0550 | 0.0178 |
| 1.16       | 806   | 806     | 100.0     | 15.82      | 12.04  | 34.13    | 0.0604 | 0.0207 |
| 1.08       | 926   | 926     | 100.0     | 12.21      | 10.47  | 26.92    | 0.0689 | 0.0274 |
| 1.01       | 825   | 825     | 100.0     | 10.36      | 8.43   | 20.57    | 0.0836 | 0.0360 |
| 0.96       | 802   | 802     | 100.0     | 9.11       | 6.40   | 15.79    | 0.1012 | 0.0477 |
| 0.92       | 951   | 951     | 100.0     | 8.19       | 5.29   | 12.76    | 0.1219 | 0.0608 |
| 0.88       | 824   | 824     | 100.0     | 7.74       | 4.66   | 10.67    | 0.1362 | 0.0715 |
| 0.85       | 649   | 649     | 100.0     | 7.55       | 4.74   | 10.39    | 0.1334 | 0.0731 |
| 0.83       | 1035  | 1035    | 100.0     | 7.24       | 4.76   | 10.02    | 0.1435 | 0.0779 |
| 0.80       | 826   | 826     | 100.0     | 7.06       | 4.48   | 9.34     | 0.1562 | 0.0857 |
| 0.78       | 832   | 832     | 100.0     | 6.78       | 4.49   | 8.99     | 0.1609 | 0.0904 |
| 0.76       | 1007  | 1007    | 100.0     | 6.61       | 3.78   | 7.62     | 0.1890 | 0.1083 |
| 0.74       | 531   | 531     | 100.0     | 6.47       | 3.57   | 7.15     | 0.2047 | 0.1180 |
| 0.73       | 1160  | 1160    | 100.0     | 6.29       | 3.06   | 6.03     | 0.2267 | 0.1402 |
| 0.71       | 630   | 630     | 100.0     | 6.10       | 2.94   | 5.60     | 0.2454 | 0.1510 |
| 0.70       | 620   | 620     | 100.0     | 5.94       | 2.67   | 5.05     | 0.2638 | 0.1687 |
| 0.69       | 839   | 1028    | 81.6      | 3.33       | 2.27   | 3.58     | 0.2749 | 0.2844 |
| 0.78       | 5619  | 5808    | 96.7      | 5.85       | 3.27   | 6.34     | 0.2100 | 0.1397 |
| Inf        | 16675 | 16864   | 98.9      | 9.92       | 9.08   | 20.53    | 0.0598 | 0.0399 |
Three low-angle reflections [1 1 3] [2 0 6] [-1 1 7] where shadowed by the beamstop and removed from the data set before the final refinement cycles. The compound is highly air- and temperature sensitive. The investigated crystal was small and the structure contains several disordered regions. One isopropyl group of the anion exhibits a 60:40 % disorder over two positions. A second isopropyl group of the cation shows a disorder over three positions with 33.3 % occupancy for each component. All three CH$_2$Cl$_2$ solute molecules are disordered over two positions with varying occupancies (50:50 %, 75:25 % and 70:30 %).

A resolution cut off of 0.75 Å was applied to exclude poor diffraction intensity data at high resolution. The atomic displacement parameters of the disordered atoms were constrained to be equal: EADP C37C C37B C37A C38B C38A C38C C36 C31 C32 C33 C34 C35 C30 and EADP C44 Cl8 Cl9. The atomic distances in disorder solute molecules have been restrained to the following target values with an estimated standard deviation of 0.02: DFIX 1.76 Cl6A C43A, DFIX 1.76 Cl7A C43A, DFIX 1.76 Cl6B C43B, DFIX 1.76 Cl7B C43B. One CH$_2$Cl$_2$ molecule could only be satisfactorily described by isotropic displacement parameters.

High residual density of 3.18 eÅ$^{-3}$ in the region of one of the octahedral coordination sites on each Ru atom in the absence of H$_2$ in the model is a potential sign for the presence of H$_2$ attached to Ru1. The quality of data set does not allow experimental localization of the attached H$_2$ molecule (see below).

**Figure S5.** The molecular structure (carbon = grey, nitrogen = blue, chlorine = dark green, ruthenium = dark blue, positive electron density = light green) of the anion with residual electron density around the Ru atoms (drawn from: difference map Olex2, total min = $-2.524$ eÅ$^{-3}$, total max. = $3.673$ eÅ$^{-3}$, 1.4 eÅ$^{-3}$ and 0.1 Å resolution). Cation, solute molecules, disorder and H-atoms have been removed for clarity.
**Supramolecular Features.** Complex 9·5(CH₂Cl₂) crystallizes in the centrosymmetric space group C2/c and the molecules are located about crystallographic special positions (two-fold rotational axes). Dense packing of the molecules can be inferred from the fact that there are no remaining voids in the unit cell (Mercury: probe radius = 1.2 Å, grid spacing = 0.7 Å).

![Figure S6. The packing of molecules relative to the unit cell viewed along the unique b-axis (left) and in a random orientation (right); H-atoms and disorder have been removed for clarity.](image1)

A short contact (3.39 Å) between C28 and Cl2 indicates an ionic interaction between [HIPr]⁺ and the diruthenium anion. There are no hydrogen bond motifs found in this structure.

![Figure S7. Ionic interaction via short contacts between C28 of [HIPr]⁺ and Cl2 of the diruthenium anion; H-atoms, solute molecules and disorder have been removed for clarity.](image2)
Refinement of the Structure with Theoretically Calculated H$_2$ Positions. Inclusion of H$_2$ at theoretically calculated positions did not significantly improve the model. The presence of H$_2$ attached to Ru was shown by NMR spectroscopy and the H–H distance found to be $\approx$ 0.94 Å. Theoretical calculations on DFT level show a H–H bond distance of 0.93 Å and where in good agreement with experimental observations. The two H-atoms were manually placed on the theoretically predicted positions at the Ru atom and restrained on these positions using EQIV and DFIX instructions: EQIV $\$1$ 1-X,+Y,0.5-Z, DFIX 1.635 0.0002 Hb Ru1, DFIX 0.93 0.0002 Ha Hb, DFIX 2.55 0.0002 Ha Cl2, DFIX 1.635 0.0002 Ha Ru1, DFIX 3.32 0.0002 Ha Cl1-$\$1$, DFIX 3.25 0.0002 Hb Cl2. Refinement by full-matrix least-squares (SHELXL) against $F^2$ with Ru–H and H–H distances fixed at 1.635 Å and 0.930 Å, respectively, resulted in $R_1 = 0.0474$ [$I > 2\sigma(I)$], $wR_2 = 0.1126$, 559 parameters and a residual electron density peak of 3.16 eÅ$^{-3}$ from Ru1 (drawn from: difference map Olex2, total min = $-2.518$ eÅ$^{-3}$, total max. = 3.648 eÅ$^{-3}$, 1.4 eÅ$^{-3}$ and 0.1 Å resolution). The H-atoms attached to Ru1 could therefore not be satisfactorily resolved from the experimental X-ray dataset.

Figure S8. The molecular structure (carbon = grey, nitrogen = blue, chlorine = dark green, ruthenium = dark blue, hydrogen = white, positive electron density = light green, q-peaks = light brown) of the anionic part of the structure with manually placed H-atoms on the theoretically predicted positions at the Ru central atom. Unrefined electron density around the Ru atoms (drawn from: difference map Olex2, total min = $-2.518$ eÅ$^{-3}$, total max. = 3.648 eÅ$^{-3}$, 1.4 eÅ$^{-3}$ and 0.1 Å resolution) indicates that the manually inserted H$_2$ moieties attached to the Ru atoms do not fully describe the residual electron density. Cationic part, solute molecules, disorders and other H-atoms are omitted for clarity.
### Table S3. Crystal Data and Structure Refinement of Complex 9-5(CH₂Cl₂).

| Property                        | Value                                |
|---------------------------------|--------------------------------------|
| Identification code             | **9·5(CH₂Cl₂)** (internal code: 13206) |
| Empirical formula               | **C₈₆H₁₂₁Cl₁₅N₆Ru₂**                  |
| Color                           | orange                               |
| Formula weight                  | 1972.77 g·mol⁻¹                      |
| Temperature                     | 100(2) K                             |
| Wavelength                      | 0.71073 Å                            |
| Crystal system                  | Monoclinic                           |
| Space group                     | C2/c, (no. 15)                       |
| Unit cell dimensions            | a = 22.8887(10) Å, b = 15.1400(6) Å, c = 27.8398(12) Å, α = 90°, β = 94.106(2)°, γ = 90° |
| Volume                          | 9622.7(7) Å³                         |
| Z                               | 4                                    |
| Density (calculated)            | 1.362 Mg·m⁻³                         |
| Absorption coefficient          | 0.775 mm⁻¹                           |
| F(000)                          | 4088 e                               |
| Crystal size                    | 0.037 x 0.032 x 0.011 mm³            |
| θ range for data collection     | 1.467 to 28.280°.                    |
| Index ranges                    | -30 ≤ h ≤ 30, -20 ≤ k ≤ 20, -37 ≤ l ≤ 37 |
| Reflections collected           | 139529                               |
| Independent reflections         | 11946 [R_{int} = 0.0543]             |
| Reflections with I>2σ(I)        | 10004                                |
| Completeness to θ = 25.242°     | 100.0 %                              |
| Absorption correction           | Gaussian                             |
| Max. and min. transmission      | 0.99056 and 0.97086                  |
| Refinement method               | Full-matrix least-squares on F²     |
| Data / restraints / parameters  | 11946 / 10 / 559                     |
| Goodness-of-fit on F²           | 1.043                                |
| Final R indices [I>2σ(I)]       | R₁ = 0.0474, wR² = 0.1126            |
| R indices (all data)            | R₁ = 0.0598, wR² = 0.1198            |
| Extinction coefficient          | n/a                                  |
| Largest diff. peak and hole     | 3.156 and -2.096 e·Å⁻³               |
Table S4. Complex 9·5(CH₂Cl₂): Bond lengths [Å] and Angles [°].

| Bond/Distance          | Value     | Bond/Distance          | Value     |
|------------------------|-----------|------------------------|-----------|
| Ru(1)-HA               | 1.6350(2) | Ru(1)-HB               | 1.6350(2) |
| Ru(1)-Cl(1)#1          | 2.5302(7) | Ru(1)-Cl(1)            | 2.4288(7) |
| Ru(1)-Cl(2)            | 2.3941(7) | Ru(1)-Cl(3)            | 2.4118(7) |
| Ru(1)-C(1)             | 2.004(3)  | N(1)-C(1)              | 1.379(4)  |
| N(1)-C(2)              | 1.386(4)  | N(1)-C(4)              | 1.449(4)  |
| N(2)-C(1)              | 1.379(3)  | N(2)-C(3)              | 1.390(4)  |
| N(2)-C(16)             | 1.439(4)  | C(2)-H(2)              | 0.9500    |
| C(2)-C(3)              | 1.341(4)  | C(3)-H(3)              | 0.9500    |
| C(4)-C(5)              | 1.400(4)  | C(4)-C(9)              | 1.396(4)  |
| C(5)-C(6)              | 1.397(4)  | C(5)-C(10)             | 1.520(5)  |
| C(6)-H(6)              | 0.9500    | C(6)-C(7)              | 1.382(5)  |
| C(7)-H(7)              | 0.9500    | C(7)-C(8)              | 1.378(5)  |
| C(8)-H(8)              | 0.9500    | C(8)-C(9)              | 1.388(4)  |
| C(9)-C(13A)            | 1.464(19) | C(9)-C(13B)            | 1.64(2)   |
| C(10)-H(10)            | 1.0000    | C(10)-C(11)            | 1.536(5)  |
| C(10)-C(12)            | 1.531(5)  | C(11)-H(11A)           | 0.9800    |
| C(11)-H(11B)           | 0.9800    | C(11)-H(11C)           | 0.9800    |
| C(12)-H(12A)           | 0.9800    | C(12)-H(12B)           | 0.9800    |
| C(12)-H(12C)           | 0.9800    | C(13A)-H(13A)          | 1.0000    |
| C(13A)-C(14A)          | 1.54(2)   | C(13A)-C(15A)          | 1.518(14) |
| C(13B)-H(13B)          | 1.0000    | C(13B)-C(14B)          | 1.51(3)   |
| C(13B)-C(15B)          | 1.53(2)   | C(14A)-H(14A)          | 0.9800    |
| C(14A)-H(14B)          | 0.9800    | C(14A)-H(14C)          | 0.9800    |
| C(14B)-H(14D)          | 0.9800    | C(14B)-H(14E)          | 0.9800    |
| C(14B)-H(14F)          | 0.9800    | C(15A)-H(15A)          | 0.9800    |
| C(15A)-H(15B)          | 0.9800    | C(15A)-H(15C)          | 0.9800    |
| C(15B)-H(15D)          | 0.9800    | C(15B)-H(15E)          | 0.9800    |
| C(15B)-H(15F)          | 0.9800    | C(16)-C(17)            | 1.398(4)  |
| C(16)-C(21)            | 1.401(4)  | C(17)-C(18)            | 1.394(4)  |
| C(17)-C(22)            | 1.518(4)  | C(18)-H(18)            | 0.9500    |
| C(18)-C(19)            | 1.379(5)  | C(19)-H(19)            | 0.9500    |
| C(19)-C(20)            | 1.389(5)  | C(20)-H(20)            | 0.9500    |
| C(20)-C(21)            | 1.388(4)  | C(21)-C(25)            | 1.522(4)  |
| Bond                  | Distance   |
|----------------------|------------|
| C(22)-H(22)          | 1.0000     |
| C(22)-C(24)          | 1.525(5)   |
| C(23)-H(23B)         | 0.9800     |
| C(24)-H(24A)         | 0.9800     |
| C(24)-H(24C)         | 0.9800     |
| C(25)-C(26)          | 1.530(5)   |
| C(26)-H(26A)         | 0.9800     |
| C(26)-H(26C)         | 0.9800     |
| C(27)-H(27B)         | 0.9800     |
| Cl(4A)-C(42)         | 1.820(17)  |
| Cl(5A)-C(42)         | 1.60(4)    |
| Cl(8)-C(44)          | 1.765(11)  |
| C(42)-H               | 1.08(5)    |
| Cl(6A)-C(43A)        | 1.770(7)   |
| Cl(7A)-C(43A)        | 1.761(6)   |
| C(43A)-HF             | 0.9900     |
| C(43B)-HH             | 0.9900     |
| N(3)-C(28)           | 1.388(4)   |
| N(3)-C(30)           | 1.454(4)   |
| C(38C)-HK             | 0.9800     |
| C(38C)-C(36)         | 1.527(12)  |
| C(28)-HM              | 0.9500     |
| C(30)-C(31)          | 1.395(4)   |
| C(31)-C(32)          | 1.396(4)   |
| C(32)-HO              | 0.9500     |
| C(33)-HP              | 0.9500     |
| C(34)-HQ              | 0.9500     |
| C(35)-C(39)          | 1.516(4)   |
| C(36)-C(37B)         | 1.519(14)  |
| C(36)-C(38B)         | 1.458(13)  |
| C(37C)-HR             | 0.9800     |
| C(37C)-HT             | 0.9800     |
| C(37B)-HV             | 0.9800     |
| C(37A)-HX             | 0.9800     |
| Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|
| C(37A)-HZ    | 0.9800     | C(38B)-H(1)  | 0.9800     |
| C(38B)-H(4)  | 0.9800     | C(38B)-H(5)  | 0.9800     |
| C(38A)-H(9)  | 0.9800     | C(38A)-H(11) | 0.9800     |
| C(38A)-H(12) | 0.9800     | C(39)-H(13)  | 1.0000     |
| C(39)-C(40)  | 1.543(4)   | C(39)-C(41)  | 1.530(4)   |
| C(40)-H(14)  | 0.9800     | C(40)-H(15)  | 0.9800     |
| C(40)-H(16)  | 0.9800     | C(41)-H(17)  | 0.9800     |
| C(41)-H(21)  | 0.9800     | C(41)-H(23)  | 0.9800     |
| HA-Ru(1)-HB  | 33.046(8)  | Cl(1)#1-Ru(1)-HA | 103.61(3) |
| Cl(1)-Ru(1)-HA | 168.37(3)  | Cl(1)#1-Ru(1)-HB | 88.40(5)  |
| Cl(1)-Ru(1)-HB | 158.02(3)  | Cl(1)-Ru(1)-Cl(1)#1 | 78.73(3)  |
| Cl(2)-Ru(1)-HA | 75.94(2)  | Cl(2)-Ru(1)-HB   | 106.00(3) |
| Cl(2)-Ru(1)-Cl(1) | 92.61(2)  | Cl(2)-Ru(1)-Cl(1)#1 | 93.38(2)  |
| Cl(2)-Ru(1)-Cl(3) | 172.85(2) | Cl(3)-Ru(1)-HA   | 108.99(3) |
| Cl(3)-Ru(1)-HB | 77.71(4)  | Cl(3)-Ru(1)-Cl(1)#1 | 80.51(2)  |
| Cl(3)-Ru(1)-Cl(1) | 82.60(2)  | Cl(1)-Ru(1)-HA   | 78.40(8)  |
| C(1)-Ru(1)-HB | 92.22(9)  | C(1)-Ru(1)-Cl(1) | 99.76(8)  |
| C(1)-Ru(1)-Cl(1)#1 | 176.98(8) | C(1)-Ru(1)-Cl(2) | 89.30(8)  |
| C(1)-Ru(1)-Cl(3) | 96.73(8)  | Ru(1)-Cl(1)-Ru(1)#1 | 82.33(2)  |
| Ru(1)#1-Cl(3)-Ru(1) | 85.20(3)  | C(1)-N(1)-C(2)  | 111.7(2)  |
| C(1)-N(1)-C(4) | 130.7(2)  | C(2)-N(1)-C(4)  | 117.5(2)  |
| C(1)-N(2)-C(3) | 112.0(2)  | C(1)-N(2)-C(16) | 128.1(2)  |
| C(3)-N(2)-C(16) | 119.9(2)  | N(1)-C(1)-Ru(1) | 131.5(2)  |
| N(1)-C(1)-N(2) | 102.4(2)  | N(2)-C(1)-Ru(1) | 126.1(2)  |
| N(1)-C(2)-H(2) | 126.3     | C(3)-C(2)-N(1)  | 107.3(3)  |
| C(3)-C(2)-H(2) | 126.3     | N(2)-C(3)-H(3)  | 126.7     |
| C(2)-C(3)-N(2) | 106.5(3)  | C(2)-C(3)-H(3)  | 126.7     |
| C(5)-C(4)-N(1) | 118.2(3)  | C(9)-C(4)-N(1)  | 118.7(3)  |
| C(9)-C(4)-C(5) | 122.7(3)  | C(4)-C(5)-C(10) | 122.8(3)  |
| C(6)-C(5)-C(4) | 117.2(3)  | C(6)-C(5)-C(10) | 120.0(3)  |
| C(5)-C(6)-H(6) | 119.4     | C(7)-C(6)-C(5)  | 121.1(3)  |
| C(7)-C(6)-H(6) | 119.4     | C(6)-C(7)-H(7)  | 119.9     |
| C(8)-C(7)-C(6) | 120.1(3)  | C(8)-C(7)-H(7)  | 119.9     |
| C(7)-C(8)-H(8) | 119.4     | C(7)-C(8)-C(9)  | 121.3(3)  |
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| C(18)-C(19)-C(20) | 120.2(3) | C(20)-C(19)-H(19) | 119.9 |
| C(19)-C(20)-H(20) | 119.5 | C(21)-C(20)-C(19) | 121.0(3) |
| C(21)-C(20)-H(20) | 119.5 | C(16)-C(21)-C(25) | 121.5(3) |
| C(20)-C(21)-C(16) | 117.5(3) | C(20)-C(21)-C(25) | 121.0(3) |
| C(17)-C(22)-H(22) | 108.0 | C(17)-C(22)-C(23) | 109.5(3) |
| C(17)-C(22)-C(24) | 112.8(3) | C(23)-C(22)-H(22) | 108.0 |
| C(24)-C(22)-H(22) | 108.0 | C(24)-C(22)-C(23) | 110.4(3) |
| C(22)-C(23)-H(23A) | 109.5 | C(22)-C(23)-H(23B) | 109.5 |
| C(22)-C(23)-H(23C) | 109.5 | H(23A)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 | H(23B)-C(23)-H(23C) | 109.5 |
| C(22)-C(24)-H(24A) | 109.5 | C(22)-C(24)-H(24B) | 109.5 |
| C(22)-C(24)-H(24C) | 109.5 | H(24A)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 | H(24B)-C(24)-H(24C) | 109.5 |
| C(21)-C(25)-H(25) | 108.2 | C(21)-C(25)-C(26) | 109.3(3) |
| C(21)-C(25)-C(27) | 113.4(3) | C(26)-C(25)-H(25) | 108.2 |
| C(27)-C(25)-H(25) | 108.2 | C(27)-C(25)-C(26) | 109.4(3) |
| C(25)-C(26)-H(26A) | 109.5 | C(25)-C(26)-H(26B) | 109.5 |
| C(25)-C(26)-H(26C) | 109.5 | H(26A)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 | H(26B)-C(26)-H(26C) | 109.5 |
| C(25)-C(27)-H(27A) | 109.5 | C(25)-C(27)-H(27B) | 109.5 |
| C(25)-C(27)-H(27C) | 109.5 | H(27A)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 | H(27B)-C(27)-H(27C) | 109.5 |
| Cl(4A)-C(42)-H | 116(3) | Cl(4A)-C(42)-HC | 106(3) |
| Cl(4B)-C(42)-Cl(5B) | 113.1(4) | Cl(4B)-C(42)-H | 106(3) |
| Cl(4B)-C(42)-HC | 111(3) | Cl(5A)-C(42)-Cl(4A) | 110.2(13) |
| Cl(5A)-C(42)-H | 96(3) | Cl(5A)-C(42)-HC | 109(3) |
| Cl(5B)-C(42)-H | 101(3) | Cl(5B)-C(42)-HC | 106(3) |
| H-C(42)-HC | 120(4) | Cl(8)-C(44)-HC | 108.3 |
| Cl(8)-C(44)-HE | 108.3 | Cl(9)-C(44)-Cl(8) | 116.1(6) |
| Cl(9)-C(44)-HD | 108.3 | Cl(9)-C(44)-HE | 108.3 |
| HD-C(44)-HE | 107.4 | Cl(6A)-C(43A)-HF | 109.5 |
| Cl(6A)-C(43A)-HG | 109.5 | Cl(7A)-C(43A)-Cl(6A) | 110.9(4) |
| Cl(7A)-C(43A)-HF | 109.5 | Cl(7A)-C(43A)-HG | 109.5 |
| HF-C(43A)-HG | 108.0 | Cl(6B)-C(43B)-HH | 109.3 |
| Cl(6B)-C(43B)-HI | 109.3 | Cl(7B)-C(43B)-Cl(6B) | 111.5(10) |
C(36)-C(38A)-H(11) 109.5  C(36)-C(38A)-H(12) 109.5
H(9)-C(38A)-H(11) 109.5  H(9)-C(38A)-H(12) 109.5
H(11)-C(38A)-H(12) 109.5  C(35)-C(39)-H(13) 107.8
C(35)-C(39)-C(40) 109.4(3)  C(35)-C(39)-C(41) 113.5(3)
C(40)-C(39)-H(13) 107.8  C(41)-C(39)-H(13) 107.8
C(41)-C(39)-C(40) 110.4(3)  C(39)-C(40)-H(14) 109.5
C(39)-C(40)-H(15) 109.5  C(39)-C(40)-H(16) 109.5
H(14)-C(40)-H(15) 109.5  H(14)-C(40)-H(16) 109.5
H(15)-C(40)-H(16) 109.5  C(39)-C(41)-H(17) 109.5
C(39)-C(41)-H(21) 109.5  C(39)-C(41)-H(23) 109.5
H(17)-C(41)-H(21) 109.5  H(17)-C(41)-H(23) 109.5
H(21)-C(41)-H(23) 109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

**Database Survey: Ru₂Cl₃X₂**

A Database (CSD Version 5.41, November 2019) survey was performed on 19th August 2020 in a search for related structures. The following search motive was used in ConQuest (Version 2020.1) program:

![Diagram]

The initial search found 28 structures containing the predefined Ru₂Cl₃X₂ entity. Twelve of them appear to be a neutral complexes with mixed Ru oxidation states of +II and +III. The remaining sixteen structures show an ionic composition with Ru oxidation states of +II. These Ru species are negatively charged and interact with a various cationic entities.
The most similar compounds are of the [Ru₂X₅L₄]⁻ type. Most of them show a cis-arrangement of the non-bridging Cl atoms relative to the Ru···Ru vector. Short contacts indicate ionic interactions between the various escorting ammonium- or phosphonium cations and the pockets formed by two bridging and the non-bridging Cl atoms. Moreover, the observed Ru···Ru distances are similar to that in 9·5(CH₂Cl₂) (3.265 Å).

However, it is pointed out that none of these known complexes contains any “vacant” coordination sites, to which H₂ could bind. Therefore their relationship to complex 9 discussed herein is merely structural rather than functional.
ZUXXEV\(^{[1]}\) Ru1-Ru1B distance = 3.331 Å

XEFTII\(^{[2]}\) Ru1-Ru2 distance = 3.271 Å; Ru3-Ru4 distance = 3.280 Å

LUSKER\(^{[3]}\) Ru1-Ru2 distance = 3.371 Å

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ICADAS$^4$ Ru1-Ru2 distance = 3.370 Å

FIJVUP$^5$ Ru1-Ru1B distance = 3.365 Å

DOSPUW$^6$ Ru1-Ru2 distance = 3.258 Å

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Database Survey: Complexes Comprising a [Ru–iPr] Unit

A Database (CSD Version 5.42, September 2021) survey was performed on January 19, 2022, searching for related structures containing a ruthenium atom bonded to an iPr ligand. The following search motive was used in ConQuest (Version 2021.2.0) program:

Searching without using predefined geometrical parameters (e.g. Ru–C distance) revealed in 58 structures but some of them are deposited without 3D coordinates. The initial search using predefined geometrical parameters found 52 structures containing the predefined Ru–(iPr) substructure. Within the dataset, 84 symmetry-independent bond lengths (caused by $Z' > 1$) are available. The average Ru–C distance is 2.098(38) Å. In complex 9, the Ru-C distance of 2.004(2) Å appears to be the shortest described so far.

Figure S9. Comparison of the [Ru–C] bond lengths of crystallographically characterized complexes comprising this substructure (CCDC code); complex 9 is highlighted in orange.
**Computed Coordinates of the Ruthenate Entity of Complex 9**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C1   | -0.5774400000 | 3.6642900000 | 1.8172100000 |
| H2   | 0.1164300000 | 3.3299700000 | 1.0335900000 |
| H3   | -0.2468300000 | 3.2259300000 | 2.7712100000 |
| H4   | -0.4989300000 | 4.7595000000 | 1.9177100000 |
| C5   | -3.6498300000 | 3.1118900000 | -1.9863000000 |
| C6   | -4.1582200000 | -1.6456100000 | 1.3875600000 |
| C7   | -3.2505500000 | 2.7636900000 | -0.6847100000 |
| C8   | -4.5029400000 | 2.2043300000 | -2.8521200000 |
| H9   | -4.5095400000 | 1.2084800000 | -2.3848600000 |
| C10  | -3.2391400000 | 0.3272900000 | 0.0964800000 |
| C11  | -2.9819300000 | 3.7185400000 | 2.5626800000 |
| H12  | -3.0275200000 | 4.8205500000 | 2.5607500000 |
| H13  | -2.6654400000 | 3.3962000000 | 3.5685300000 |
| C14  | -4.0012400000 | 3.3394400000 | 2.3946800000 |
| C15  | -4.6807900000 | -2.7361000000 | 0.6638100000 |
| C16  | -5.9433100000 | 2.7153800000 | -2.9420900000 |
| H17  | -6.4151500000 | 2.7959900000 | -1.9503200000 |
| H18  | -6.5575000000 | 2.0314500000 | -3.5501900000 |
| H19  | -5.9860600000 | 3.7123400000 | -3.4124400000 |
| C20  | -5.2633700000 | -2.5693300000 | -0.7265500000 |
| H21  | -4.8452500000 | -1.6442700000 | -1.1532100000 |
| C22  | -4.2056700000 | -0.1054600000 | 4.4603400000 |
| H23  | -5.1332500000 | 0.1691200000 | 3.9365100000 |
| C24  | -3.8522200000 | 0.7842400000 | 5.0059900000 |
| H25  | -4.4554200000 | -0.8816300000 | 5.2027900000 |
| C26  | -2.0623500000 | 4.8357200000 | -0.4378900000 |
| H27  | -1.4289100000 | 5.5054800000 | 0.1468900000 |
| C28  | -3.2353700000 | 4.3533900000 | -2.4821300000 |
| C29  | -3.5243200000 | 4.6442000000 | -3.4948400000 |
| C30  | -6.7875000000 | -2.4334500000 | -0.6625600000 |
| H31  | -7.2001600000 | -2.2728700000 | -1.6713800000 |
| H32  | -7.0979100000 | -1.5832900000 | -0.0364900000 |
| H33  | -7.2524700000 | -3.3436100000 | -0.2469800000 |
| C34  | -4.1571400000 | -4.1590700000 | 2.5638700000 |
| H35  | -4.1515000000 | -5.1507600000 | 3.0242500000 |
| C36  | -1.8256800000 | -0.8956900000 | 4.2269400000 |
| H37  | -1.9562900000 | -1.6532200000 | 5.0170300000 |
| H38  | -1.4570700000 | 0.0213200000 | 4.7123700000 |
| H39  | -1.0467100000 | -1.2363900000 | 3.5303000000 |
| C40  | -4.8548800000 | -3.6885200000 | -1.6811100000 |
| H41  | -3.7610200000 | -3.7863500000 | -1.7303000000 |
| H42  | -5.1997600000 | -3.4486700000 | -2.6979400000 |
| H43  | -5.2903700000 | -4.6626100000 | -1.4013000000 |
| C44  | -4.6669900000 | -3.9912500000 | 1.2814700000 |
| H45  | -5.0589700000 | -4.8549500000 | 0.7400300000 |
| C46  | -2.4570500000 | 5.2110000000 | -1.7177700000 |
| H47  | -2.1402700000 | 6.1742700000 | -2.1267300000 |
| C48  | -3.8965500000 | 2.0097400000 | -4.2411200000 |
| H49  | -3.8966600000 | 2.9426900000 | -4.8294300000 |
| H50  | -4.4792700000 | 1.2616800000 | -4.8010400000 |
| Atom | X coordinate | Y coordinate | Z coordinate |
|------|--------------|--------------|--------------|
| C105 | 4.1589700000 | 4.1571200000 | 2.5668700000 |
| H106 | 4.1536700000 | 5.1485500000 | 3.0278200000 |
| C107 | 1.8251400000 | 0.8940800000 | 4.2272700000 |
| H108 | 1.9560000000 | 0.8940800000 | 4.7120400000 |
| C109 | 3.6885200000 | 1.2356700000 | 3.5306600000 |
| H110 | 1.9560000000 | 1.6510500000 | 5.0178600000 |
| H111 | 1.4558700000 | -0.0230000000 | 4.7120400000 |
| C112 | 3.7864800000 | -1.7279500000 | 3.0278200000 |
| H113 | 5.2037100000 | 3.4492100000 | -2.6948700000 |
| C114 | 5.2936600000 | 4.6623800000 | -1.3974700000 |
| H115 | 4.6693300000 | 3.6885200000 | -1.7197100000 |
| H116 | 4.2137500000 | -6.1728000000 | -2.1291600000 |
| C117 | 5.0620800000 | 5.1485500000 | 3.0278200000 |
| H118 | 5.0620800000 | 5.1485500000 | 3.0278200000 |
| H119 | 5.9132700000 | -2.0070800000 | -4.2415800000 |
| H120 | 3.9395700000 | -2.9395700000 | -4.8306300000 |
| C121 | 4.2576200000 | -1.5285600000 | -4.8012800000 |
| H122 | 2.8642600000 | -1.6304700000 | -4.1591000000 |
| C123 | 3.6413400000 | 1.7881800000 | 2.6925500000 |
| C124 | 3.6413400000 | 1.7881800000 | 2.6925500000 |
| H125 | 1.9867500000 | -2.1136700000 | 1.5353700000 |
| C126 | 5.0569300000 | -1.6651300000 | 0.4833600000 |
| C127 | 5.6393700000 | -2.5796700000 | 0.4289100000 |
| C128 | 5.3253000000 | -0.4701800000 | 1.0486400000 |
| H129 | 6.1931000000 | 3.0656000000 | 3.2619100000 |
| C130 | 3.6509400000 | 3.0656000000 | 3.2619100000 |
| C131 | 3.2501900000 | 3.2062600000 | 4.2682400000 |
| C132 | 3.1296800000 | 0.6014000000 | 3.4897000000 |
| C133 | 2.9179300000 | -0.2071100000 | 2.7744500000 |
| C134 | 2.4444000000 | -3.6084300000 | 0.1041300000 |
| C135 | 0.5140200000 | -1.5201200000 | -1.5703600000 |
| C136 | 2.8173600000 | 0.8933000000 | -2.6480700000 |
| N137 | 4.2210300000 | 0.3317900000 | 0.8207800000 |
| N138 | 3.7957800000 | -1.5779500000 | -0.0822400000 |
| Ru139 | 1.5810400000 | 0.4793900000 | -0.6251900000 |
| H140 | 1.9522100000 | 1.7205500000 | 0.3770600000 |
| H141 | 2.0688300000 | 2.0309300000 | -0.4909800000 |
**General**

All reactions were carried out under argon in flame-dried glassware, ensuring rigorously inert conditions. The solvents were purified by distillation over the indicated drying agents and were stored and handled under argon: CH$_2$Cl$_2$ (CaH$_2$), MeCN (CaH$_2$), pentane (Na/K alloy), THF (Na/K alloy).

Hydrogen gas (N50, ≥99.999 Vol.%) was purchased from AirLiquide and was used without further purification. Deuterium hydride (HD) (96 mol% DH, 98% atom % D) was purchased from Sigma-Aldrich. Hydrogen and HD were handled with standard balloon techniques.

NMR spectra were recorded on Bruker AVIII 400, AVIII 500 or AVneo 600 MHz NMR spectrometers at 298 K unless otherwise indicated; chemical shift (δ) given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD$_2$Cl$_2$: 5.32 ppm (1H), 53.8 ppm (13C); [D$_3$]-MeCN: 1.94 ppm (1H), 118.26 ppm (13C); [D$_6$]-acetone: 2.05 ppm (1H), 29.8 ppm (13C).

IR spectra: Alpha Platinum ATR (Bruker) at room temperature, wavenumbers (ν) are given in cm$^{-1}$.

Mass spectrometry: MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Bruker ESQ3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan); GC-MS: Shimadzu GCMS-QP2010 Ultra instrument.

Photolysis experiments: PhotoRedOxBox TC (HepatoChem) equipped with an EvoluChem™ LED (365 nm, 18 W) (Figure S10). When the cooling function was used, water was the cooling agent (23 °C).

*Figure S10. PhotoRedOxBox TC (HepatoChem)*
Hydride Intermediates

Figure S11. Hydride region of the $^1$H NMR ([D$_8$]-toluene) spectrum recorded at the end of the light-driven *gem*-hydrogenation of enyne 6 with formation of cyclopentene 7

**Complex 9.** In a flame-dried quartz Schlenk tube under argon, [(IPr)Ru(p-cymene)Cl$_2$]$_1$ (1b)$_1$ (134 mg, 192 µmol) and IPrHCl (163 mg, 385 µmol) were suspended in toluene (15 mL). The Schlenk tube was closed with a septum and then transferred into the PhotoRedOxBox. A hydrogen-filled balloon was connected to a needle, which was pierced through the septum. The Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). The exit cannula was removed but the hydrogen-filled balloon remained attached to the Schlenk tube to ensure constant hydrogen pressure throughout the reaction. The light
source was switched on and the reaction mixture was stirred for 20 min under hydrogen atmosphere. After this time, the yellow suspension was filtered via a filter cannula into another Schlenk tube and the filtrate was concentrated in vacuum. The remaining material was washed with pentane (3 x 10 mL). Drying under high vacuum afforded the title compound (110 mg, 73%) as a yellow solid. Orange crystals suitable for X-ray diffraction were grown by slow cooling of a saturated solution in CH$_2$Cl$_2$:C$_6$F$_6$ (1:1, v/v) from +20 to −50°C over the course of 2 weeks.

$^1$H NMR (600 MHz, 233 K, THF-[D$_8$]) $\delta$ 9.10 (s, 2H), 8.86 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.36 (d, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 6.5$ Hz, 2H), 7.31 (d, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.7$ Hz, 2H), 7.14 (s, 2H), 7.10 (t, $J = 7.4$ Hz, 2H), 6.96 (d, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 7.5$ Hz, 2H), 6.84 (s, 2H), 3.31 (hept, $J = 6.6$ Hz, 2H), 2.96 (hept, $J = 6.6$ Hz, 2H), 2.85 (hept, $J = 6.6$ Hz, 2H), 2.80 (hept, $J = 6.6$ Hz, 2H), 2.61 (hept, $J = 6.6$ Hz, 2H), 2.33 (hept, $J = 6.6$ Hz, 2H), 1.33 (d, $J = 6.3$ Hz, 6H), 1.31 (d, $J = 6.3$ Hz, 6H), 1.24 (d, $J = 6.5$ Hz, 6H), 1.08 (d, $J = 6.5$ Hz, 6H), 1.06 (d, $J = 6.9$ Hz, 6H), 1.00 (s, 12H), 0.97 (d, $J = 6.5$ Hz, 6H), 0.91 – 0.86 (m, 12H), 0.82 (d, $J = 6.5$ Hz, 6H), 0.45 (d, $J = 5.9$ Hz, 6H), −11.54 (s, 4H). $^{13}$C NMR (151 MHz, 233 K, THF-[D$_8$]) $\delta$ 189.6, 148.9, 148.2, 147.5, 146.8, 146.7, 146.3, 140.7, 140.5, 135.7, 132.0, 131.7, 131.0, 129.7, 128.5, 127.4, 124.9, 124.8, 124.5, 124.3, 124.2, 123.6, 123.0, 67.4, 29.4, 29.3, 29.2, 29.1, 28.5, 28.4, 26.8, 26.4, 26.2, 25.3, 24.4, 23.9, 23.8, 23.4, 23.2, 23.0, (two signals missing due to overlap with solvent signals, see assignment-table on the next page). IR (film) $\tilde{\nu}$ 3068, 2963, 2928, 2867, 2125, 1534, 1465, 1447, 1387, 1290, 1261, 1102, 953, 933, 801, 756, 697, 443 cm$^{-1}$. Anal. (%) calcd for C$_{81}$H$_{112}$Cl$_5$N$_6$Ru$_2$C$_{62}$.80, H 7.29, Cl 11.43, N 5.42, Ru 13.04; found: C 61.57, H 7.39, Cl 11.07, N 5.29, Ru 12.61.

$^1$H NMR (400 MHz, 298 K, toluene-[D$_8$]) $\delta$ 9.27 (d, $J = 1.9$ Hz, 2H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.28 (q, $J = 6.2$, 4.8 Hz, 5H), 7.17 (dd, $J = 6.2$, 2.6 Hz, 12H), 6.53 (bs, 4H), 6.24 (t, $J = 1.8$ Hz, 1H), 3.30 (ddt, $J = 18.0$, 13.4, 6.8 Hz, 4H), 3.15 (t, $J = 6.9$ Hz, 4H), 2.57 (p, $J = 6.8$ Hz, 2H), 2.34 (p, $J = 6.8$ Hz, 2H), 1.35 (d, $J = 6.7$ Hz, 8H), 1.26 (d, $J = 6.5$ Hz, 18H), 1.17 (d, $J = 6.8$ Hz, 8H), 1.09 (d, $J = 6.8$ Hz, 14H), 1.07 – 1.00 (m, 12H), 0.94 (dd, $J = 9.1$, 6.9 Hz, 12H), −11.26 (s, 4H).

$^1$H NMR (400 MHz, 298 K, CD$_2$Cl$_2$) $\delta$ 8.73 (s, 2H), 7.85 (s, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.39 – 7.28 (m, 9H), 7.20 (d, $J = 7.7$ Hz, 4H), 7.11 (s, 3H), 6.82 (s, 4H), 3.01 – 2.89 (m, 4H), 2.81 (p, $J = 6.7$ Hz, 4H), 2.43 (p, $J = 6.6$ Hz, 4H), 1.33 (d, $J = 6.3$ Hz, 14H), 1.05 (dd, $J = 13.5$, 6.6 Hz, 30H), 0.91 (dd, $J = 7.1$, 4.7 Hz, 28H), −11.86 (s, 4H). $^{13}$C NMR (101 MHz, 298 K, CD$_2$Cl$_2$) $\delta$ 188.5, 148.3, 146.9, 146.0, 139.7, 131.7, 130.8, 128.8, 124.7, 123.6, 28.9, 28.5, 28.3, 26.3, 25.6, 23.6, 23.0, 23.0.
NMR data supports the following structure

observed HMBC cross peaks

A few comments to the structure:
- Sample was measured at -40°C as at higher temperatures only broad signals were observed.
- At -40°C there are multiple EXSY peaks visible in the 2D ROESY, e.g. H10 <> H110, H18 <> H108, H16 <> H106, but not between protons on the same ring (e.g. H18 and H16).
- This can either be explained by a rotation around the C1-Ru bond or more likely a flip on of the birping C1.
- Intermolecular NOEs (e.g. H201 <> H105 and H-203<>16/106) show the close spacial proximity of the cation and the anion in solution.
- Due to the exchange of the two sites in the cation, some NOEs might be explained by the chem. exchange as well (e.g. H14 sees H105). Therefore also the assignment of CH100 and CH10 might be exchangeable. Due to probe limitations on the cryoprobe the sample could not be cooled further.
- The sample might contain some minor amount of free NHC ligand.
Deuterium-Labelled Ruthenate α-HD complex [D₂]-9. In a flame-dried quartz Schlenk tube under argon, [(IPr)Ru(ρ-cymene)Cl₂] (1b) (119 mg, 171 µmol) and IPrHCl (145 mg, 342 µmol) were suspended in toluene (15 mL). The Schlenk tube was closed with a septum and then transferred into the PhotoRedOxBox. A balloon filled with H–D gas was connected to a needle, which was pierced through the septum. The Schlenk tube was flushed with HD for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). The exit cannula was removed but the balloon remained attached to the Schlenk tube to ensure constant pressure of HD gas throughout the reaction. The light source was switched on and the reaction mixture was stirred for 20 min under HD atmosphere. After this time, the yellow suspension was filtered via a filter canula into another Schlenk tube and the filtrate was concentrated in vacuum. The remaining material was washed with pentane (3 x 10 mL). Drying under high vacuum afforded the title compound (101 mg, 76%) as a yellow solid.

1H NMR (400 MHz, CD₂Cl₂) δ 8.53 (s, 2H), 7.91 (s, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.37 – 7.29 (m, 9H), 7.20 (d, J = 7.8 Hz, 4H), 7.16 – 7.08 (m, 3H), 6.81 (s, 4H), 2.96 – 2.88 (m, 4H), 2.88 – 2.77 (m, 4H), 2.53 – 2.39 (m, 4H), 1.35 (d, J = 6.2 Hz, 14H), 1.05 (dd, J = 9.8, 6.5 Hz, 30H), 0.91 (dd, J = 7.4, 4.3 Hz, 28H), –11.91 (t, J = 29.4 Hz, 2H). 13C NMR (101 MHz, CD₂Cl₂) δ 188.6, 148.3, 146.9, 146.0, 139.7, 131.7, 130.8, 128.8, 124.7, 123.6, 28.9, 28.5, 28.3, 26.3, 25.6, 23.6, 23.0, 23.0.

As can be seen in Figure S12, the 1:1:1 triplet in the hydride region of this complex is not perfectly symmetrical because of overlapping signal of undeuterated 9. From the recorded ¹J_HD = 29.4 Hz of [D₂]-9 one can deduced the following H–H distances (d_H,H) for the ligated H₂ molecule:

\[ d_{HH} = 1.42 - 0.0167J_{HD} \] (Morris et al.)

\[ d_{HH} = 1.44 - 0.0168J_{HD} \] (Heinekey et al.)
Figure S12. Hydride region of the $^1$H NMR spectra (CD$_2$Cl$_2$) of [D$_2$]-9 (top) and unlabeled 9 (bottom).

**Complex 8.** In a flame-dried Schlenk tube under argon, [(IPr)(p-cymene)RuCl$_2$]$_2$ (1b) (100 mg, 143 µmol) was dissolved in toluene (15 mL). The Schlenk tube was closed with a septum and a hydrogen-filled balloon was connected to a needle, which was pierced through the septum. The Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). The exit cannula was removed but the hydrogen-filled balloon remained attached to the Schlenk tube to ensure constant hydrogen pressure throughout the reaction. The mixture was heated to 90 °C for 1 h under a hydrogen atmosphere in the dark. After this time, the red solution was evaporated *in vacuo*. The remaining material was suspended in pentane and filtered with a filter canula into another Schlenk flask. The filtrate was concentrated in vacuum to provide the title compound as a red crystalline solid (34 mg, 42%). Red
crystals suitable for X-ray diffraction were grown upon slowly cooling a saturated pentane solution from room temperature to −20 °C.

$^1$H NMR (600 MHz, toluene-[D$_8$]) δ 7.29 (t, $J = 7.7$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.14 (dd, $J = 7.7$, 1.5 Hz, 2H), 6.61 (s, 2H), 4.83 (t, $J = 5.5$ Hz, 1H), 4.64 (d, $J = 5.8$ Hz, 1H), 4.35 (d, $J = 5.5$ Hz, 1H), 4.15 (t, $J = 5.5$ Hz, 1H), 3.63 (td, $J = 5.1$, 0.8 Hz, 1H), 3.34 (hept, $J = 7.0$ Hz, 2H), 2.93 (hept, $J = 7.0$ Hz, 2H), 1.75 (s, 3H), 1.34 (d, $J = 6.8$ Hz, 7H), 1.33 (d, $J = 6.7$ Hz, 6H), 1.05 (d, $J = 6.9$ Hz, 6H), 0.98 (d, $J = 6.9$ Hz, 6H), −6.06 (s, 1H). $^{13}$C NMR (151 MHz, toluene-[D$_8$]) δ 190.0, 146.8, 146.7, 139.0, 123.4, 123.3, 106.9, 93.4, 86.1, 82.6, 79.8, 66.7, 28.4, 28.1, 26.0, 25.5, 22.8, 22.0, 18.6.

NMR data supports the following structure:

All the observed NOE cross correlation peaks and multiple HMBC agree with the given structure. Remarkably, the hydride H22 shows HMBC to the tolyl ligand and C1 and NOE crosspeaks to the iPr groups. The 13C shifts of the toluene are all below 100 ppm indicating their coordination to the Ru.

VT measurements show broadening if the iPr groups at lower temperature

The structure could be additionally confirmed in the solid state by X-ray crystallography.

| Atom | δ (ppm) | J | COSY | HSQC | HMBC | NOESY |
|------|---------|---|------|------|------|-------|
| C1   | 125.07  | 1` | 2, 22|      |      |       |
| C2   | 123.42  | 2` | 2    |      |      |       |
| H    | 6.61    | 2` | 1, 1 | 9, 10, 12, 14 |      |       |
| C3   | 129.02  | 5` | 7, 9 |      |      |       |
| C4   | 146.85  | 6` | 9, 10, 11 |      |      |       |
| C5   | 123.68  | 5` | 7, 9 |      |      |       |
| H    | 7.14    | 1` | 5, 7, 9, 10, 11 |      |      |       |
| C6   | 129.35  | 5` |      |      |      |       |
| H    | 7.29    | 5` | 5, 7, 6, 4, 8 |      |      |       |
| C7   | 123.35  | 5` | 5    |      |      |       |
| H    | 7.21    | 5` | 5, 7, 13, 14 |      |      |       |
| C8   | 146.77  | 5` | 6, 13, 14 |      |      |       |
| C9   | 18.13   | 5` | 5, 15, 11 |      |      |       |
| H    | 2.93    | 5` | 10, 11 | 3, 4, 5, 10, 11, 2, 10, 12, 19, 22 |      |       |
| C10  | 126.07  | 5` | 10, 9, 11 |      |      |       |
| H3   | 1.05    | 5` | 10, 9, 11 | 2, 5, 9, 11 |      |       |
| C11  | 22.88   | 5` | 9, 10  |      |      |       |
| H3   | 1.34    | 5` | 11 | 9, 10, 19, 25, 22 |      |       |
| C12  | 28.43   | 5` | 12 | 7, 13, 14 |      |       |
| H    | 3.34    | 5` | 13, 14 | 12, 2, 9, 13, 19, 20, 22 |      |       |

Protein/Protein

| Atom | δ (ppm) | J | COSY | HSQC | HMBC | NOESY |
|------|---------|---|------|------|------|-------|
| C13  | 22.05   | 1` |       |      |      |       |
| H3   | 3.33    | 5` | 12, 14 | 7, 12, 14, 15, 16, 20, 21, 22 |      |       |
| C14  | 25.35   | 1` |       |      |      |       |
| H3   | 0.98    | 5` | 12, 14 | 6, 12, 14, 15, 13, 14 |      |       |
| C15  | 79.82   | 1` |       |      |      |       |
| H    | 4.83    | 5` | 16, 20 | 15, 17, 19, 20, 13, 16, 20, 22 |      |       |
| C16  | 82.61   | 1` |       |      |      |       |
| H    | 4.35    | 5` | 15, 16 | 18, 20, 21, 15, 21, 22 |      |       |
| C17  | 106.93  | 1` |       |      |      |       |
| H    | 93.43   | 5` | 15, 19, 21, 22 |      |      |       |
| C18  | 19.39   | 1` |       |      |      |       |
| H    | 5.5s(19) | 19 | 18, 19, 20 |      |      |       |
| C19  | 86.12   | 1` |       |      |      |       |
| H    | 4.15    | 5` | 18, 20, 21, 19, 17, 18, 19, 9, 11, 18, 20 |      |       |
| C20  | 60.73   | 1` |       |      |      |       |
| H    | 1.63    | 5` | 15, 19 | 15, 16, 18, 19, 11, 12, 15, 16, 21, 22 |      |       |
| C21  | 18.66   | 1` |       |      |      |       |
| H    | 1.75    | 5` | 21 | 18, 17, 18, 12, 16, 18, 22 |      |       |
| C22  | 4.06    | 1` |       |      |      |       |

Experiments: 1H-eg30, 13C-eg30, {13C, 1H}-hopedetgaipears2A, {13C, 1H}-hopedetgaipears2B, {13C, 1H}-hopedetgaipears3A, {13C, 1H}-hopedetgaipears3B, {1H, 1H}-epi core3, 1H-eg30, 1H-eg14, {1H, 1H}-noesyppph, 1H-eg30
**Kinetic Profiling.** The catalytic performance of complexes 8 and 9 was evaluated by means of the standard hydrogenative metathesis reaction of enyne 6. In case of complex 8, presence of cyclopentene 7 in the resulting complex crude reaction mixture could not be confirmed.

A flame-dried quartz Schlenk tube was charged with 9 (77.6 mg, 0.05 mmol, 20 mol%) [or 1b (69.6 mg, 0.1 mmol, 20 mol%)], enyne 6 (110 mg, 0.5 mmol) and toluene (5 mL). The Schlenk tube was closed with a septum and then transferred into the PhotoRedOxBox TC, cooled to approx. 23 °C. A hydrogen-filled balloon was connected to a needle, which was pierced through the septum. The Schlenk tube was flushed with hydrogen for 2 min through an outlet cannula (the cannula did not reach into the solution to ensure that only the head space of the tube was flushed). The exit cannula was removed but the hydrogen-filled balloon remained attached to the Schlenk tube to ensure constant hydrogen pressure throughout the reaction. The light source was switched on and samples were taken manually with oven-dried syringes every 2 mins; the samples were filtered through a short pad of silica and the filtrates analyzed by GC-MS.

![Figure S13](image)  
**Figure S13.** Formation of product 7 by light-driven hydrogenative metathesis of enyne 6 catalyzed by complex 1b (blue) or complex 9 (red)

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**T₁(min) Measurements.** The temperature-dependent T₁ relaxation times of complex 9 were measured on four different instruments (Bruker AvanceIII-300 MHz WB, Bruker AvanceIIIHD-400 MHz, Bruker AvanceIII-500 MHz, Bruker AvanceNeo 600 MHz NMR spectrometers). Temperatures for the variable temperature (VT) experiments from –60 to RT (25°C) were calibrated with 4% MeOH in [D₄]-MeOH using the implemented “calctemp” function in Bruker Topspin 3.6.1 or Topspin 4.1.2 (AVneo). Temperatures above RT were calibrated with an 80% glycol in [D₆]-DMSO.

The spin-lattice relaxation times (T₁) were determined with the inversion recovery sequence (Bruker pulse program: t1ir) using 32 non-linear spaced inversion times ranging from 0.001 ms to approx. 5 * T₁, which were adjusted individually to the different field strengths. The pulse offset during the measurement was set on-resonance on the hydride signal (≈ –11 ppm). The obtained 2D datasets were analyzed with the Bruker TOPSPIN T1T2 module by integrating the hydride signal and fitting it to the following equation:

\[ I(\tau) = I_0 + P \cdot e^{-\tau/T_1} \]

\( I_0 \) describes the magnetization at thermal equilibrium, \( \tau \) is the individual inversion time at each step in the 2D sequence, \( P \) is the polarization at \( t = 0 \).

Morris et al. developed equations that can be used to calculate an upper and lower limit of \( d_{HH} \), depending on whether the H₂ ligand is spinning slower or faster than the spectrometer frequency:

\[ d_{HH}^{slow} = 5.81 \cdot 6 \cdot \sqrt{\frac{T_1(min)}{v}} \]
\[ d_{HH}^{fast} = 4.61 \cdot 6 \cdot \sqrt{\frac{T_1(min)}{v}} \]

v = spectrometer frequency in MHz

Application of the T₁(min) method to complex 9 finds a value of 11.773 ms (300 MHz). This value corresponds to a \( d_{HH} = 0.85 – 1.06 \text{ Å} \), depending on the rotational regime of the H₂ ligand. When the lower (0.85 Å) and the upper (1.06 Å) limit of \( d_{HH} \) are compared with the value obtained by the \(^1J_{HD}\) method (0.94 Å) it can be deduced that the H₂ ligand is neither in the slow spinning nor in the fast spinning regime (see below).

More recently, Morris et al. have put forward a criterion to classify a H₂ complex into the slow or fast spinning regime:

\[ \frac{d_{HH}^{from J(HD)}}{581.5 \cdot 6 \cdot \sqrt{\frac{T_1(min)}{v}}} = 1.0 \text{ (if slow) or 0.794 (if fast)} \]
Applying this equation to the obtained data of 9, a value of 0.89 is obtained. According to Morris, $d_{HH}$ of complexes that fall between the values of 1.0 and 0.794 can be calculated by taking the average of $d_{HH}^{slow}$ and $d_{HH}^{fast}$. The average value of 0.96 Å is in excellent agreement with the value of 0.94 Å obtained by the $^1J_{HD}$ method.

Examination of the ln($T_1$)/$T^1$ plot provides further evidence for the proposed rotational regime of 9: ln($T_1$)/$T^1$ plots for slow or fast spinning H$_2$ complexes are usually V-shaped with a sharp minimum. However, the shown plot exhibits an unusually broad minimum. Complexes with such distorted ln($T_1$)/$T^1$ plots are suggestive of H$_2$ ligands that have a frequency of motion near the $^1$H Larmor frequency and hence $d_{HH}$ is between the values calculated from the $T_1$(min) value for fast spinning and slow spinning extremes.

Raw data:

| $T$ (K) | 1/T | 300 MHz | 400 MHz | 500 MHz | 600 MHz |
|--------|-----|---------|---------|---------|---------|
|        |  $T_1$ (ms) | $R_1$ (s') | ln ($T_1$) | $T_1$ (ms) | $R_1$ (s') | ln ($T_1$) | $T_1$ (ms) | $R_1$ (s') | ln ($T_1$) |
| 213    | 4.69E-03 | 33.92E-06 | -3.38E-03 | 1.69E-01 | 3.34E-04 | -2.43E-03 | 7.59E-04 | 1.03E-01 | -2.96E-03 |
| 218    | 4.59E-03 | 27.90E-06 | -3.97E-03 | 1.45E-01 | 4.68E-04 | -3.10E-03 | 8.45E-04 | 1.54E-01 | -2.73E-03 |
| 223    | 4.48E-03 | 22.77E-06 | -3.79E-03 | 1.24E-01 | 3.80E-04 | -2.34E-03 | 5.45E-04 | 1.83E-01 | -2.80E-03 |
| 228    | 4.38E-03 | 19.72E-06 | -3.92E-03 | 1.11E-01 | 3.41E-04 | -2.81E-03 | 5.06E-04 | 2.03E-01 | -3.02E-03 |
| 233    | 4.29E-03 | 17.49E-06 | -4.04E-03 | 1.01E-01 | 3.97E-04 | -2.97E-03 | 4.28E-04 | 2.33E-01 | -3.16E-03 |
| 238    | 4.20E-03 | 15.54E-06 | -4.10E-02 | 9.21E-02 | 2.70E-04 | -3.62E-02 | 3.83E-04 | 2.65E-02 | -3.26E-02 |
| 243    | 4.12E-03 | 15.11E-06 | -4.12E-02 | 8.37E-02 | 2.33E-04 | -3.62E-02 | 3.43E-04 | 2.96E-02 | -3.36E-02 |
| 248    | 4.03E-03 | 14.13E-06 | -4.25E-02 | 7.53E-02 | 2.18E-04 | -3.82E-02 | 3.13E-04 | 3.24E-02 | -3.49E-02 |
| 253    | 3.95E-03 | 13.13E-06 | -4.33E-02 | 6.77E-02 | 2.09E-04 | -3.90E-02 | 2.84E-04 | 3.54E-02 | -3.55E-02 |
| 258    | 3.88E-03 | 12.69E-06 | -4.36E-02 | 6.16E-02 | 1.98E-04 | -4.02E-02 | 2.64E-04 | 3.85E-02 | -3.63E-02 |
| 263    | 3.80E-03 | 12.24E-06 | -4.40E-02 | 5.62E-02 | 1.88E-04 | -4.19E-02 | 2.54E-04 | 4.15E-02 | -3.68E-02 |
| 268    | 3.73E-03 | 11.96E-06 | -4.46E-02 | 5.16E-02 | 1.78E-04 | -4.36E-02 | 2.44E-04 | 4.46E-02 | -3.73E-02 |
| 273    | 3.66E-03 | 11.87E-06 | -4.43E-02 | 5.06E-02 | 1.69E-04 | -4.39E-02 | 2.34E-04 | 4.77E-02 | -3.78E-02 |
| 278    | 3.60E-03 | 11.77E-06 | -4.44E-02 | 5.02E-02 | 1.61E-04 | -4.42E-02 | 2.24E-04 | 5.09E-02 | -3.83E-02 |
| 283    | 3.53E-03 | 11.62E-06 | -4.41E-02 | 4.96E-02 | 1.54E-04 | -4.45E-02 | 2.15E-04 | 5.32E-02 | -3.87E-02 |
| 288    | 3.47E-03 | 12.05E-06 | -4.19E-02 | 4.80E-02 | 1.48E-04 | -4.48E-02 | 2.06E-04 | 5.55E-02 | -3.91E-02 |
| 293    | 3.41E-03 | 12.29E-06 | -4.40E-02 | 4.85E-02 | 1.42E-04 | -4.48E-02 | 2.07E-04 | 5.79E-02 | -3.95E-02 |
| 298    | 3.35E-03 | 12.68E-06 | -4.36E-02 | 4.99E-02 | 1.38E-04 | -4.49E-02 | 2.08E-04 | 6.04E-02 | -4.00E-02 |
| 303    | 3.29E-03 | 13.10E-06 | -4.33E-02 | 5.14E-02 | 1.34E-04 | -4.50E-02 | 2.09E-04 | 6.29E-02 | -4.05E-02 |
| 308    | 3.23E-03 | 13.58E-06 | -4.29E-02 | 5.29E-02 | 1.31E-04 | -4.51E-02 | 2.10E-04 | 6.54E-02 | -4.10E-02 |
| 313    | 3.18E-03 | 14.19E-06 | -4.25E-02 | 5.46E-02 | 1.29E-04 | -4.52E-02 | 2.11E-04 | 6.79E-02 | -4.15E-02 |
| 318    | 3.14E-03 | 14.72E-06 | -4.21E-02 | 5.63E-02 | 1.27E-04 | -4.53E-02 | 2.12E-04 | 7.04E-02 | -4.20E-02 |

\[
\begin{array}{cccccc}
B_0 (T) & \nu_1 (MHz) & \nu_1 \text{max} (MHz) & \Delta \nu_1 (MHz) & \Delta B_0 (MHz) & \Delta \nu_1 \text{max} (MHz) \\
7.05 & 300.13 & 11.77 & 0.85 & 0.94 & 0.94 \\
9.39 & 400.13 & 15.85 & 0.85 & 0.94 & 0.94 \\
11.73 & 499.87 & 19.83 & 0.85 & 0.94 & 0.94 \\
14.09 & 600.20 & 24.50 & 0.86 & 0.94 & 0.94 \\
\end{array}
\]
Solid State NMR

An attempt was made to determine the distance between the two hydrogen atoms via static solid-state NMR spectroscopy. In principle, the internuclear distance can be calculated directly from the dipolar coupling, which can be obtained from the Pake doublet line shape, as has been pointed out by Zilm et al. Unfortunately, our attempts to detect the Pake pattern in static measurements of samples of 9 at 600 MHz between 100 K and room temperature were unsuccessful. In fact, even under MAS conditions (10 kHz) we were not able to detect a signal of the H2 ligand, owing to the broad lines of the proton signals in the solid state.

DFT Calculations

The geometry of complex 9 was optimized with the Gaussian 09 program, using the PBE0 functional. Ru was represented by the quasi-relativistic effective core from the Stuttgart group and the associated basis sets. The remaining atoms (H, C, N, and Cl) were represented by a double-ζ, Def2-SVP basis set. A pruned (99,590) grid was used for the geometry optimization.

The SCF density was calculated with ADF 2014, using the PBE0 functional and a Slater-type basis set of double-ζ quality (DZ). The density was visualized with the ADFView program.
$^1$H NMR of Complex 9, 600 MHz, THF-$[D_8]$, $-40 \, ^\circ\text{C}$
1H NMR spectra measured at different temperatures

1H, 1D

-40 °C

-20 °C

0 °C

25 °C

1H (ppm)
$^{13}$C NMR of Complex 9, 151 MHz, THF-$[D_8]$ at $-40 \degree$C
Overlapping with solvent signals in 1D 13C
NOEs between the cation and anion are indicating their close spacial proximity.
$^1$H NMR of Complex 9, 400 MHz, CD$_2$Cl$_2$, 23 °C
$^{13}$C NMR of Complex 9, 101 MHz, CD$_2$Cl$_2$, 23 °C
$^1$H NMR of Complex 9, 400 MHz, toluene-[D$_8$], 23 °C
Stacked $^1$H NMR spectra of Complex 9, top (toluene-$[D_8]$), bottom (CD$_2$Cl$_2$)
$^1$H NMR of Labelled Complex [D$_2$]-9, 400 MHz, CD$_2$Cl$_2$, 23 °C
$^{13}$C NMR of Labelled Complex [D$_2$]-9, 101 MHz, CD$_2$Cl$_2$, 23 °C
$^1$H NMR of Complex 8, 600 MHz, Toluene-[D$_8$], 23 °C
$^{13}$C NMR of Complex 8, 151 MHz, Toluene-[D$_8$], 23 °C

$^{13}$C NMR spectrum showing chemical shifts.
1H,13C-HMBC
$H_{22}' = I_0 + P \exp(-X/T_1)$

$I_0 = 9.836e+6; P = -1.785e+7; T_1 = 1.784$; 

Error: $1.818e+5$

The relaxation time of $H_{21}$ is $1.78s$.

H22

H22'
1H NMR spectra at different temperatures

-40°C
-30°C
-20°C
-10°C
0°C
10°C
25°C
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