Electronic Supplementary Material (ESI) for Chemical Communications

"A bis(trialkylphosphine) ruthenium (η^5-3-phenylindenyl) complex via alcoholysis"

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SUPPORTING INFORMATION

General considerations:

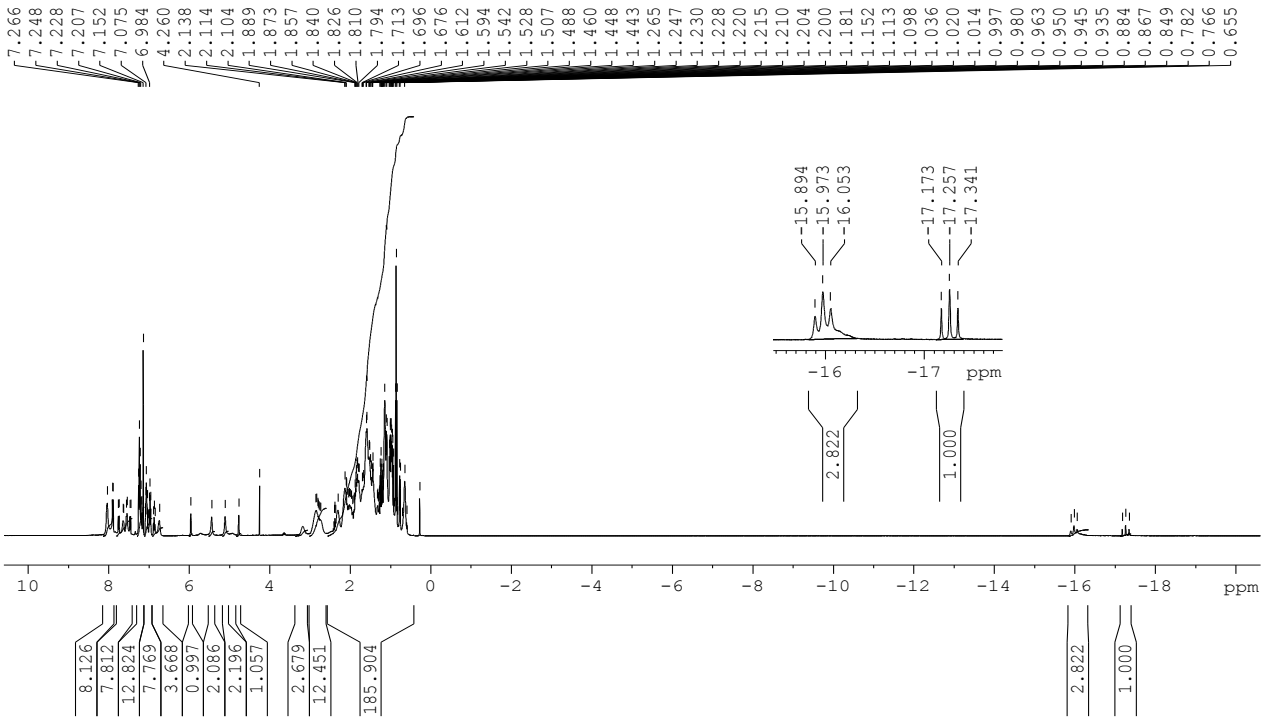
Ethanol and *iso*-propanol were purchased as anhydrous from Sigma-Aldrich and used as supplied. Pentane was degassed and distilled from $MgSO_4$. Triethylamine was purchased from Acros Organics and used as supplied. $\mathbf{M_{10}}$, $\mathbf{M_{11}}$, and $\mathbf{M_1}$ were purchased from Umicore AG. Elemental analyses were performed at the London Metropolitan University. Catalysts syntheses were performed in an MBraun glovebox containing dry argon and less than 1 ppm oxygen. ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 300 or Bruker Avance 500 Ultrashield NMR spectrometers.

Decomposition Experiments. General Procedure:

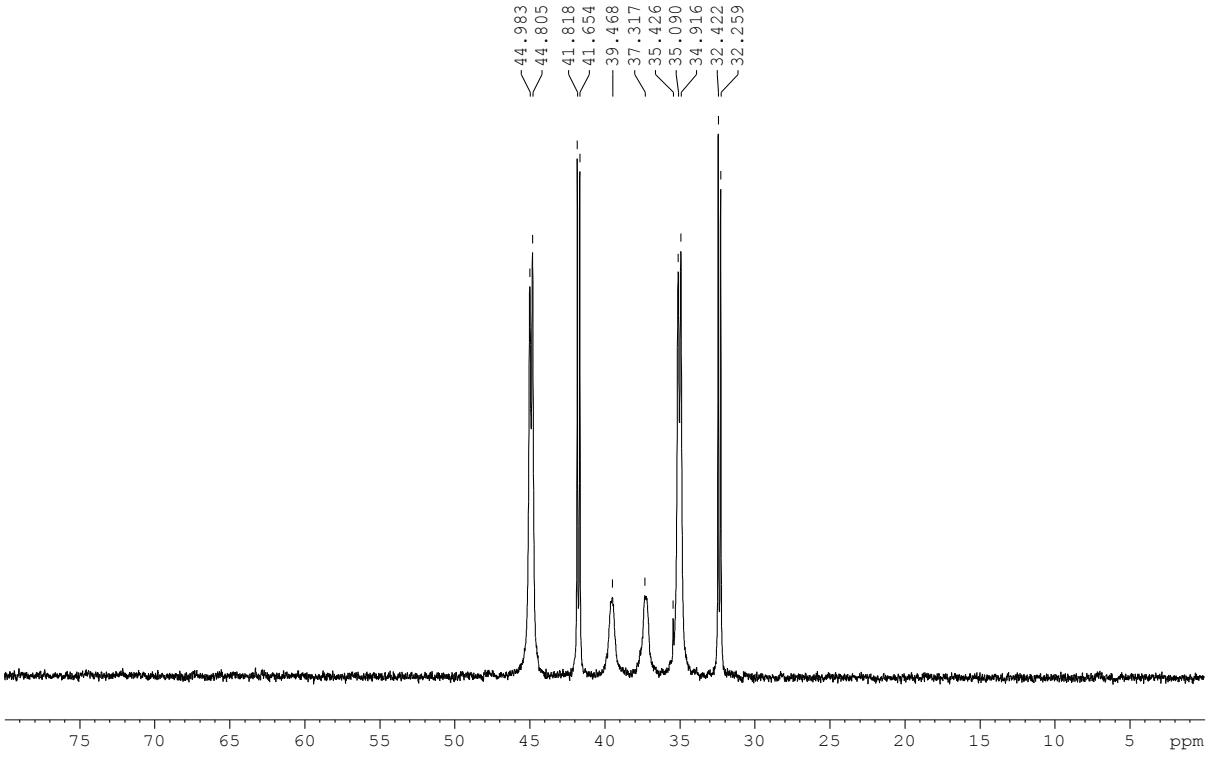
In the glovebox, the pre-catalyst was weighed (*ca.* 0.25 mmol) into a PTFE septum fitted vial and the appropriate solvent was added (3 mL). Outside of the glovebox, triethylamine (0.5 mL, 3.5 mmol) was added. The vial was then heated to reflux overnight, cooled to room temperature and, inside the glovebox, the contents were worked up and analysed by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. NMR spectra from each experiment are provided herein; experimental details are provided below where yields were recorded.

[RuH(Phob)$_2$(η^5-3-phenylindenyl)] 4. The reaction mixture (in *iso*propanol) was evaporated under vacuum. To the crude oil, pentane was added and the solution was filtered through celite. The mother liquor was evaporated until one third of the original volume, which was then cooled to -38°C. Red crystals were obtained by decanting the mother liquor, washing the solid with cold pentane and drying it *in vacuo* (137 mg, 76% yield). Complex **4** has been obtained as a mixture of three rotamers (see EXSY experiments). Anal. Calcd for $C_{39}H_{57}RuCl_2P_2$: C, 68.00; H, 8.34. Found: C, 67.88; H, 8.41.

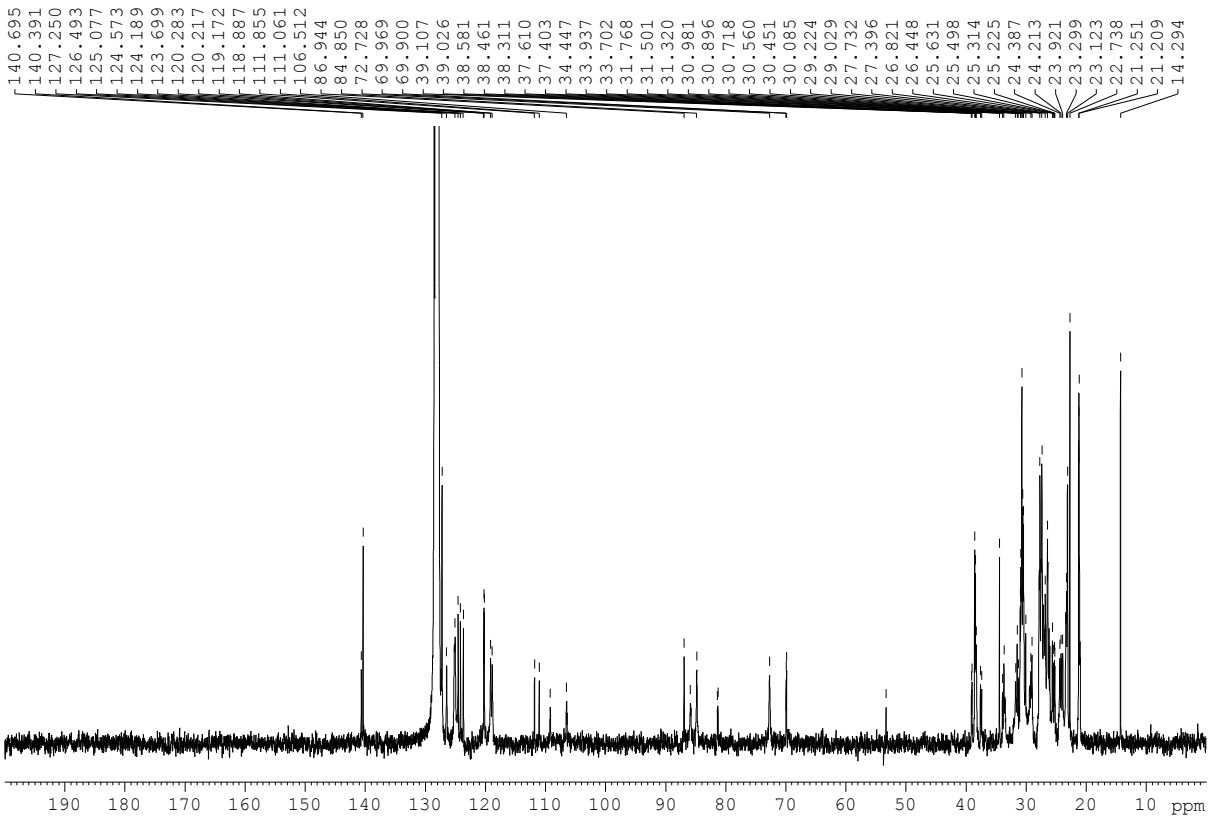
^{1}H NMR in C_6D_6



$^{31}P\{^{1}H\}$ NMR in C_6D_6

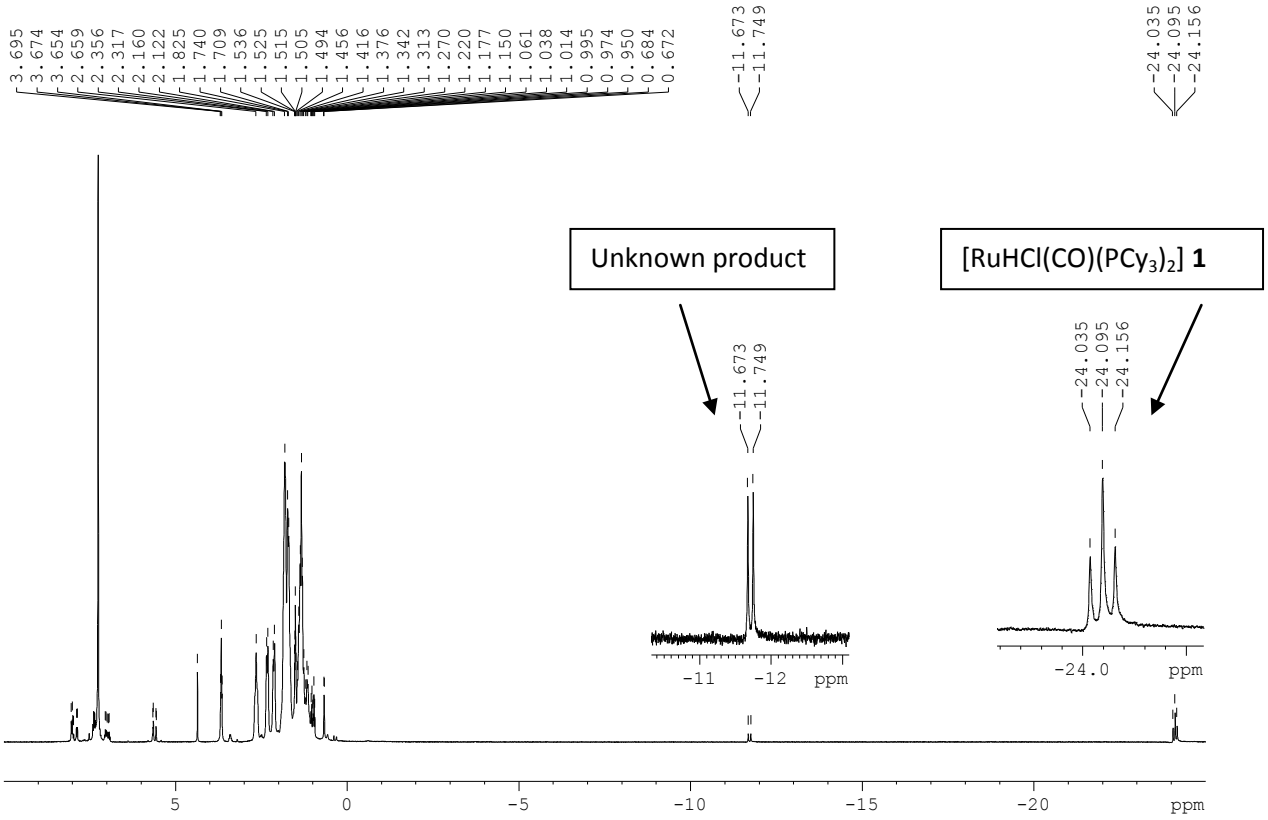


$^{13}C\{^{1}H\}$ NMR in C_6D_6

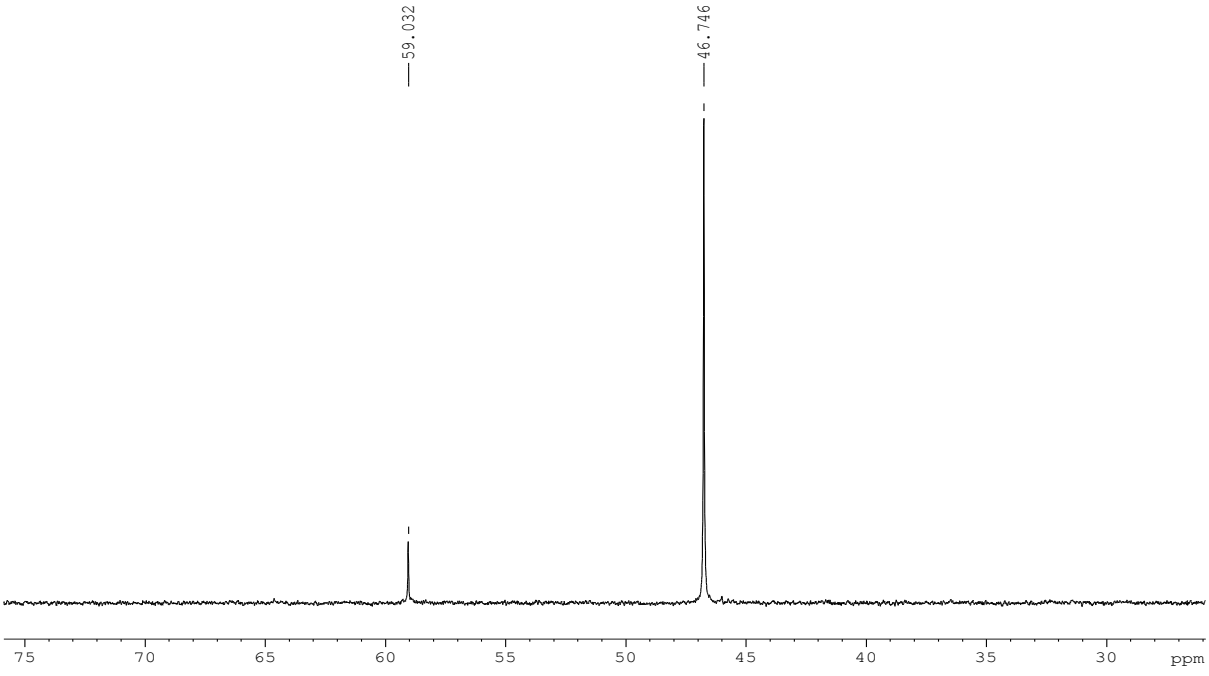


Decomposition of M_1 in EtOH: The yellow precipitate in the reaction mixture (in ethanol) was recovered by filtration and washed with cold ethanol, then pentane, and then dried under vacuum. The solid was predominantly the hydridocarbonyl complex **1**, plus traces of an unknown product.

^{1}H NMR in C_6D_6 of the yellow solid.

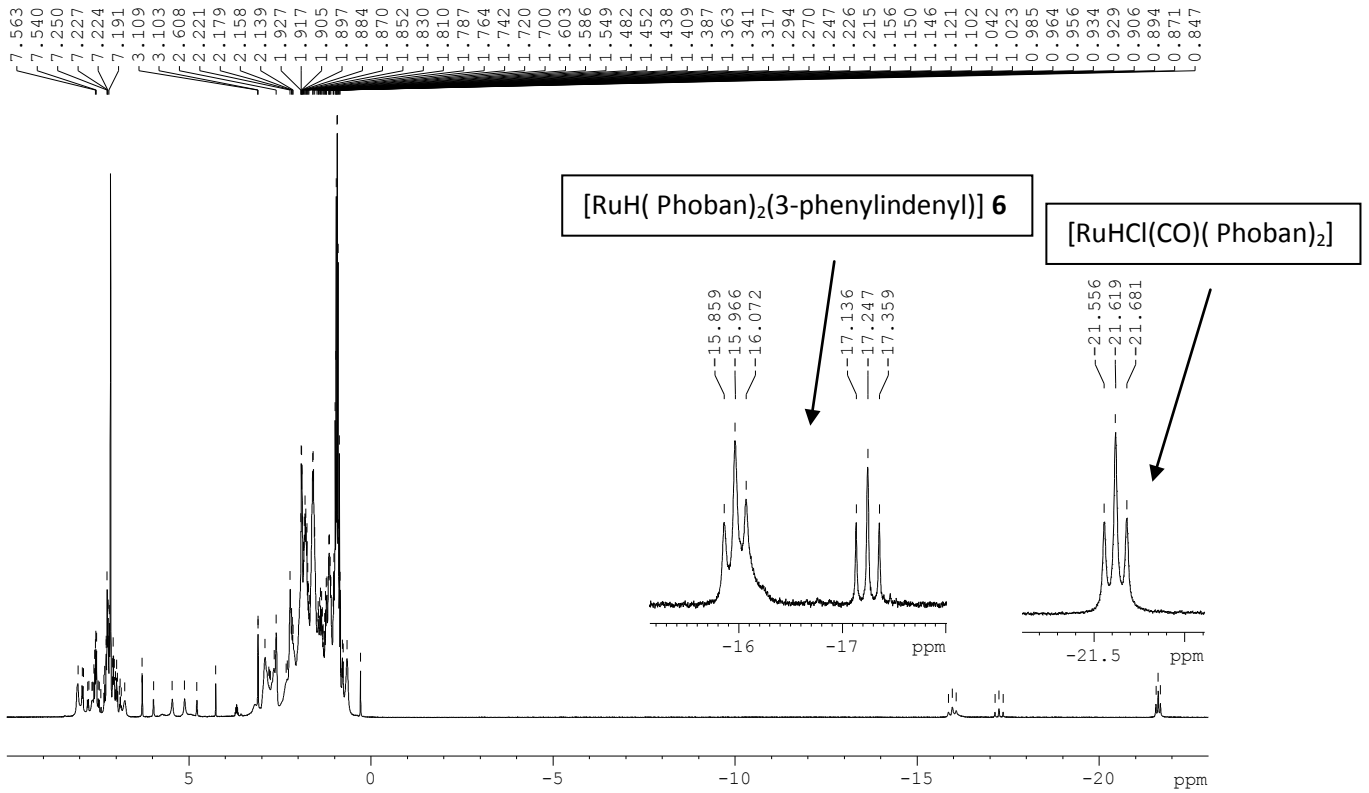


^{31}P{^{1}H} NMR in C_6D_6 of the yellow solid

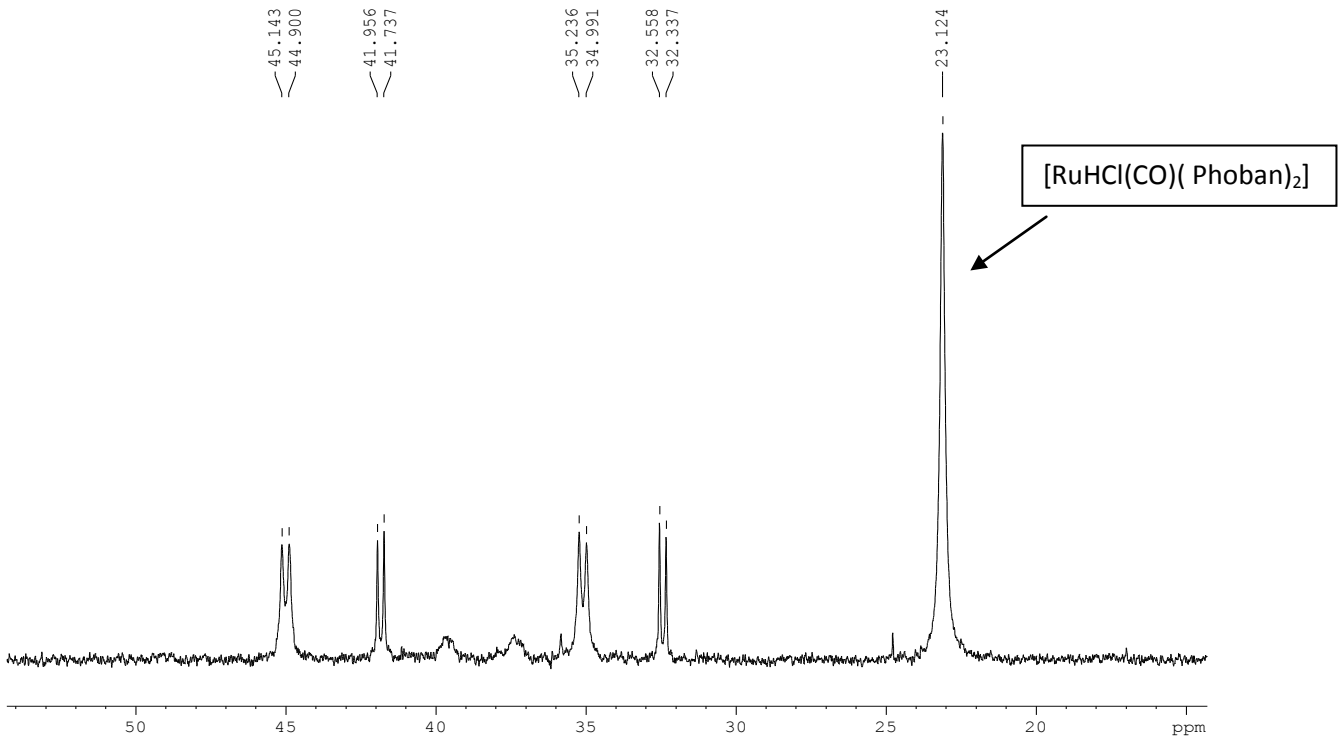


Decomposition of M_{11} in EtOH: Using the previously reported procedure for the synthesis of complex **4**, 150 mg of red powder was obtained, consisting of a 1:1 mixture of complex **6** and presumably other (presumably hydride) derivatives of $\mathbf{M_{11}}$. The signals are consistent with analogous complexes reported in the literature.

^{1}H NMR in C_6D_6 of the final crop

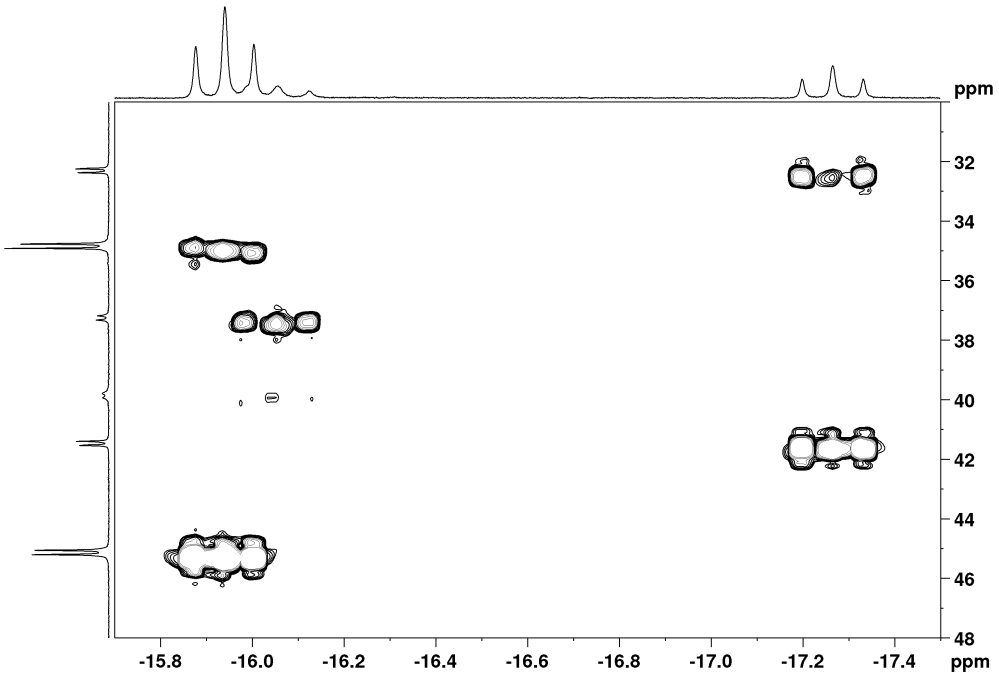


^{1}H NMR in C_6D_6 of the final crop

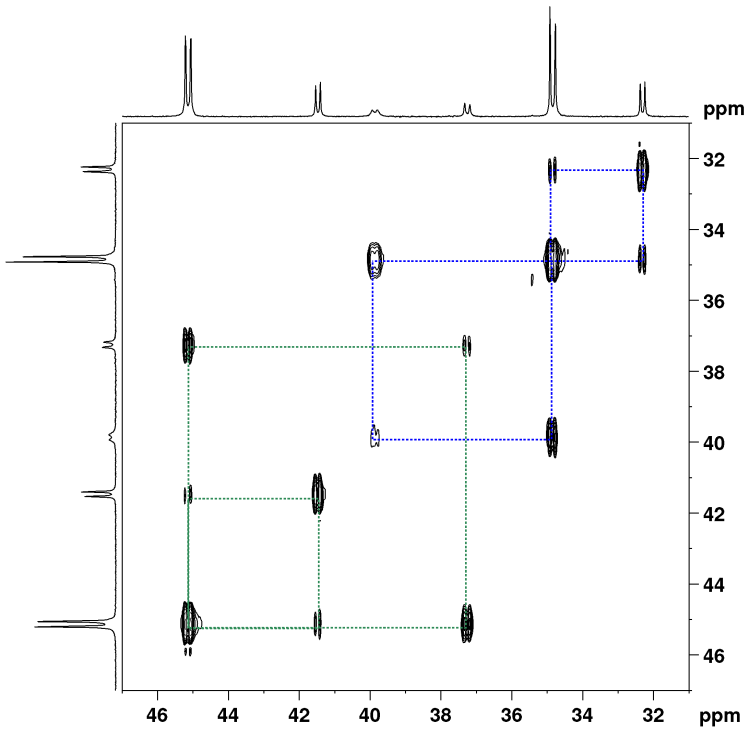


NMR Experiments

NMR experiments were conducted using a Bruker AV500 NMR spectrometer equipped with a QNP (^{1}H, ^{13}C, ^{19}F, ^{31}P) probe (500 MHz ^{1}H observe frequency; 202 MHz ^{31}P observe frequency). Chemical shifts are reported relative to external standards Me_4Si (δ_H = 0 ppm) and 85% H_3PO_4 in H_2O (δ_P = 0 ppm).



2D ^{1}H,^{31}P-HMBC spectrum of **4** optimised for J_{HP} = 30 Hz recorded at 265 K. Three hydride triplets are resolved showing correlations with three pairs of doublets in the ^{31}P dimension, implying the existence of three conformers in solution.



2D ^{31}P-EXSY spectrum of **4** recorded at 265 K showing an exchange pattern of ^{31}P resonances that complements the ^{1}H,^{31}P-HMBC correlation and supports the hypothesis about three conformers in solution. In accordance with theoretical calculations, the spectrum shows that the most abundant conformer (δ_P = 35 and 45 ppm) exchanges with less abundant ones (δ_P = 32, 40, 37 and 41, respectively).

DFT Calculations

All DFT static calculations were performed at the GGA level with the Gaussian09 set of programs,[1] using the BP86 functional of Becke and Perdew.[2] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarisation function of Ahlrichs and co-workers for H, C, N, O, and Cl (SVP keyword in Gaussian).[3] For Ru we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keyword in Gaussian09).[4] The geometry optimisations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The reported energies have been optimised via single point calculations on the BP86 geometries with triple zeta valence plus polarisation (TZVP keyword in Gaussian) using the M06L functional,[5] however estimating solvent effects with the polarizable continuous solvation model PCM using CH_2Cl_2 as the solvent.[6] Furthermore, diffuse basis sets have been incorporated for O and Cl.[7]

1. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2. (a) A. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100. (b) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824. c) J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406-7406.

3. A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys*., 1992, **97**, 2571-2577.

4. (a) U. Haeusermann, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys*., 1993, **78**, 1211-1224. (b) W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys*., 1994, **100**, 7535-7542. (c) T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, *J. Chem. Phys*., 1996, **105**, 1052-1059.

5. (a) Y. Zhao, D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101 –194118. (b) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215 –241.

6. (a) V. Barone, M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001. (b) J. Tomasi, M. Persico, *Chem. Rev.*, 1994, **94**, 2027-2094.

7. D. Rappoport, F. Furche, *J. Chem. Phys*., 2010, **133**, 134105.

Conformer 1:

E_g(BP86/SVP) = -2297.632227
G_g(BP86/SVP) = -2296.848079
E_s(M06L//TZVP) = -2299.109913
E_s(M06L//TZVP//BP86/SVP) = -2298.325765

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TS 1-2:

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E_s(M06L//TZVP//BP86/SVP) = -2298.300692

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Conformer 2:

E_g(BP86/SVP) = -2297.6312318
G_g(BP86/SVP) = -2296.846825
E_s(M06L//TZVP) = -2299.1061078
E_s(M06L//TZVP//BP86/SVP) = -2299.106108

Ru	-0.068338	0.150992	-0.662233
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P	-2.287889	-0.382877	-0.313739
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C	1.797330	0.711531	-1.956683
C	1.447835	2.059577	-1.483349
C	2.174558	3.067313	-0.787012
C	1.580105	4.311929	-0.548677
C	0.257619	4.593611	-0.972850
C	-0.492609	3.617902	-1.640653
C	0.089019	2.355019	-1.910553
C	3.134376	0.079112	-2.027841
C	3.257580	-1.318169	-2.255590
C	4.510785	-1.925651	-2.418297
C	5.691215	-1.161887	-2.340282

C	5.591552	0.221319	-2.117931
C	4.334786	0.833880	-1.973170
C	0.022977	-0.543471	3.090976
C	-0.775028	0.750248	3.391680
C	0.035418	2.056853	3.524121
C	1.064921	2.276181	2.397649
C	1.991405	1.073594	2.093685
C	2.887661	0.633542	3.277794
C	2.174577	0.013599	4.506130
C	1.005311	-0.959484	4.213150
C	2.159416	-1.741178	1.319620
C	1.702915	-3.142738	0.859930
C	0.790588	-3.858379	1.870883
C	2.933525	-4.017769	0.551068
C	-2.732119	-2.044846	0.495784
C	-2.082668	-3.186806	-0.324966
C	-2.515215	-3.315128	-1.803465
C	-2.570331	-1.987424	-2.592349
C	-3.284496	-0.809460	-1.883402
C	-4.786545	-1.052421	-1.591426
C	-5.133563	-2.159769	-0.565265
C	-4.257409	-2.212473	0.709181
C	-3.414750	0.794885	0.651932
C	-3.259942	2.307588	0.392607
C	-3.900689	2.730339	-0.940407
C	-3.861523	3.116568	1.557839
H	-1.356816	1.141403	-3.176760
H	0.667160	-0.651139	-3.368385
H	-0.719574	-1.362509	2.969177
H	-1.510692	0.884842	2.572796
H	-1.372124	0.590552	4.318503
H	-0.676368	2.911382	3.524053
H	0.534543	2.100640	4.513748
H	0.529951	2.538521	1.458623
H	1.696334	3.159310	2.644780
H	2.654594	1.368231	1.253686
H	3.466292	1.522490	3.619463
H	3.654021	-0.073415	2.894875
H	1.807286	0.827666	5.161893
H	2.931364	-0.522847	5.119727
H	1.405786	-1.966822	3.974809
H	0.420628	-1.096458	5.151912
H	2.894156	-1.350032	0.580507
H	2.702056	-1.836913	2.282766
H	1.132584	-3.007082	-0.087770
H	1.321762	-4.037230	2.831554
H	-0.128899	-3.281373	2.095486
H	0.471922	-4.848942	1.483630
H	3.592858	-3.542120	-0.203020
H	2.630316	-5.013898	0.163894
H	3.540287	-4.188509	1.467643
H	-2.246621	-2.038322	1.497336
H	-2.279813	-4.151810	0.194996
H	-0.984857	-3.035113	-0.289799
H	-3.496641	-3.827418	-1.868352
H	-1.803225	-3.998896	-2.315857
H	-3.071369	-2.170504	-3.570030
H	-1.535144	-1.660525	-2.827930
H	-3.217942	0.069304	-2.560045
H	-5.289068	-1.296760	-2.555589
H	-5.241487	-0.091600	-1.269493
H	-5.095949	-3.146191	-1.068791
H	-6.196052	-2.036752	-0.260158
H	-4.429519	-3.191485	1.212853
H	-4.605553	-1.450437	1.438181
H	-4.479495	0.508617	0.525672
H	-3.168611	0.576523	1.714170
H	-2.170311	2.535853	0.341718
H	-3.446434	2.203251	-1.804285
H	-3.785793	3.820829	-1.114691
H	-4.991159	2.510184	-0.945609
H	-3.740519	4.208270	1.393272
H	-4.949795	2.914487	1.669467
H	-3.375060	2.866201	2.524006
H	-1.512128	3.837024	-1.991654
H	-0.177935	5.586924	-0.781344
H	2.157699	5.091683	-0.026332
H	3.203387	2.886703	-0.444789
H	2.344462	-1.933047	-2.291389
H	4.568538	-3.010503	-2.604293
H	6.675874	-1.641029	-2.459109
H	6.502580	0.840128	-2.073004
H	4.285000	1.925752	-1.860261
H	0.086973	-1.401594	-0.826014

TS 1-3:

E_g(BP86/SVP) = -2297.612372
G_g(BP86/SVP) = -2296.824526
E_s(M06L//TZVP) = -2299.088547
E_s(M06L//TZVP//BP86/SVP) = -2298.300701

Ru	0.032350	-0.684725	-0.044568
P	-0.702889	1.540791	-0.017133
P	2.316769	-0.370136	-0.500992
C	0.187017	-2.778370	0.754182
C	-0.722477	-2.734741	-0.350332
C	-1.921337	-2.021498	0.043299
C	-1.766664	-1.694433	1.465404
C	-2.635349	-1.105537	2.432570
C	-2.242952	-1.064172	3.774031
C	-0.975248	-1.542345	4.197126
C	-0.078622	-2.080531	3.266802
C	-0.471729	-2.188802	1.909824
C	-3.157610	-2.060613	-0.770149
C	-3.082565	-2.130662	-2.187583
C	-4.235420	-2.253348	-2.975025
C	-5.507959	-2.302328	-2.373815
C	-5.602791	-2.240248	-0.973718
C	-4.446298	-2.127289	-0.182678
C	-2.574367	1.874694	-0.070456
C	-3.139870	1.345274	-1.411241
C	-2.584568	1.971395	-2.707833
C	-1.049194	2.113619	-2.741695
C	-0.397830	2.724898	-1.476017
C	-0.828840	4.179714	-1.162274
C	-2.308850	4.398044	-0.768490
C	-2.906002	3.361866	0.212121
C	-0.084438	2.503584	1.487097
C	-0.323157	1.878190	2.885227

C	-1.663998	2.302112	3.508767
C	0.837341	2.241102	3.831756
C	2.933860	-1.586466	-1.854498
C	2.761487	-3.034084	-1.334435
C	3.520981	-3.404530	-0.032767
C	3.537310	-2.345227	1.100241
C	3.746837	-0.876917	0.666017
C	5.146889	-0.613689	0.050667
C	5.480364	-1.333484	-1.276367
C	4.372750	-1.311046	-2.355957
C	2.950924	1.247057	-1.276285
C	3.019087	2.603429	-0.530967
C	3.922102	2.640587	0.713269
C	3.451662	3.698619	-1.527865
H	1.092849	-3.387865	0.805538
H	-0.609631	-3.278867	-1.296714
H	-3.030383	1.264022	0.738067
H	-2.957071	0.255098	-1.442482
H	-4.246687	1.463787	-1.395403
H	-2.900252	1.333445	-3.562204
H	-3.056797	2.957302	-2.896980
H	-0.594866	1.110809	-2.901547
H	-0.756942	2.733032	-3.620355
H	0.693566	2.739698	-1.659366
H	-0.604029	4.805708	-2.056455
H	-0.167977	4.576385	-0.361300
H	-2.927780	4.429196	-1.687228
H	-2.410393	5.411177	-0.320741
H	-2.597505	3.608514	1.248397
H	-4.015002	3.469659	0.206486
H	1.009261	2.557976	1.316642
H	-0.451690	3.551333	1.468878
H	-0.326283	0.770315	2.772141
H	-1.719222	3.407312	3.627383
H	-2.531548	1.976803	2.901199
H	-1.787312	1.853476	4.516011
H	1.808653	1.869269	3.443288
H	0.686061	1.798006	4.838663
H	0.924772	3.342980	3.960292
H	2.236897	-1.457436	-2.711120
H	3.087163	-3.732431	-2.138589
H	1.678214	-3.213203	-1.207893
H	4.566239	-3.673718	-0.285787
H	3.085673	-4.346193	0.371616
H	4.342396	-2.615555	1.820945
H	2.593700	-2.385836	1.679927
H	3.654292	-0.253139	1.580732
H	5.908933	-0.906607	0.809539
H	5.280606	0.478215	-0.081247
H	5.756636	-2.385185	-1.062315
H	6.402947	-0.879494	-1.700729
H	4.614410	-2.080329	-3.125034
H	4.396805	-0.347616	-2.906928
H	3.957182	1.045123	-1.692482
H	2.285758	1.366224	-2.161093
H	1.996348	2.861628	-0.192066
H	3.627533	1.887944	1.471842
H	3.864808	3.637466	1.198842
H	4.988470	2.466963	0.454294
H	3.465514	4.698953	-1.045685
H	4.474463	3.501229	-1.917447
H	2.769644	3.755355	-2.402646
H	0.903871	-2.462682	3.587464
H	-0.698468	-1.487796	5.261575
H	-2.934867	-0.643471	4.521258
H	-3.620388	-0.714447	2.139676
H	-2.095800	-2.058536	-2.672067
H	-4.141657	-2.302224	-4.072137
H	-6.414965	-2.391720	-2.992453
H	-6.589094	-2.294270	-0.484647
H	-4.545003	-2.129151	0.912208
H	-0.016492	-0.511480	-1.614607

Conformer 3:

E_g(BP86/SVP) = -2297.6297002
G_g(BP86/SVP) = -2296.843627
E_s(M06L//TZVP) = -2299.1031381
E_s(M06L//TZVP//BP86/SVP) = -2298.317065

Ru	0.050817	-0.527091	-0.551949
P	-0.855739	0.868232	1.108601
P	2.300659	0.091535	-0.732420
C	0.269987	-2.382042	-1.788248
C	-0.791124	-1.552751	-2.275429
C	-1.894637	-1.580683	-1.329228
C	-1.536036	-2.566567	-0.296348
C	-2.235383	-3.104083	0.820993
C	-1.640417	-4.105996	1.597894
C	-0.345136	-4.595881	1.303465
C	0.376082	-4.078205	0.219959
C	-0.205719	-3.073325	-0.592239
C	-3.235803	-1.047550	-1.662584
C	-3.371612	0.041226	-2.565392
C	-4.630874	0.488239	-2.990380
C	-5.805748	-0.123201	-2.512682
C	-5.694244	-1.199206	-1.617202
C	-4.431824	-1.659997	-1.205766
C	0.094112	1.866954	2.419960
C	0.995542	0.881909	3.204251
C	0.288686	-0.232895	4.003040
C	-0.789557	-0.989651	3.201726
C	-1.803254	-0.099528	2.442809
C	-2.663861	0.804840	3.359942
C	-1.929172	1.945624	4.107670
C	-0.850326	2.715249	3.306131
C	-2.220532	2.009386	0.474581
C	-1.909002	3.102516	-0.571857
C	-1.137248	4.300351	0.007838
C	-3.219744	3.598214	-1.214126
C	3.429606	-1.168057	-1.622153
C	3.549819	-2.429662	-0.734144
C	4.212383	-2.239379	0.647167
C	3.667560	-1.033573	1.439300
C	3.586730	0.306621	0.664119
C	4.946427	0.843743	0.150453
C	5.679641	0.008507	-0.927865
C	4.796428	-0.581016	-2.053507
C	2.543810	1.587276	-1.860531
C	1.889977	2.936170	-1.493213

C	2.648985	3.693686	-0.390446
C	1.758105	3.815427	-2.751732
H	1.166869	-2.651921	-2.357697
H	-0.826891	-1.082890	-3.266392
H	0.769605	2.562747	1.876529
H	1.662654	0.396644	2.465479
H	1.654430	1.465626	3.886842
H	1.058677	-0.961978	4.338905
H	-0.144525	0.176871	4.938206
H	-0.292829	-1.653903	2.461079
H	-1.351505	-1.664661	3.886030
H	-2.490687	-0.775428	1.893194
H	-3.159077	0.151447	4.114652
H	-3.497581	1.226114	2.759366
H	-1.468500	1.537862	5.029377
H	-2.685769	2.676293	4.469165
H	-1.333804	3.481864	2.667070
H	-0.224869	3.292207	4.025706
H	-2.938635	1.285194	0.029422
H	-2.740577	2.477886	1.335570
H	-1.290116	2.633792	-1.371467
H	-1.749560	4.835201	0.766899
H	-0.186002	4.003374	0.491592
H	-0.890964	5.034378	-0.788048
H	-3.789047	2.767006	-1.675833
H	-3.019185	4.357573	-1.999794
H	-3.876773	4.073899	-0.452768
H	2.888914	-1.459684	-2.549332
H	4.099021	-3.216509	-1.300378
H	2.527375	-2.819134	-0.565446
H	5.313709	-2.163362	0.544701
H	4.042024	-3.160694	1.246386
H	4.284467	-0.883167	2.354023
H	2.643192	-1.286018	1.794347
H	3.181219	1.066231	1.365738
H	5.625299	0.957258	1.027264
H	4.790342	1.876081	-0.226101
H	6.236439	-0.813878	-0.436465
H	6.466005	0.645121	-1.389776
H	5.368097	-1.390612	-2.563097
H	4.626390	0.183985	-2.839996
H	3.623747	1.750318	-2.053844
H	2.106349	1.225533	-2.817769
H	0.864278	2.718100	-1.126348
H	2.720439	3.107981	0.548901
H	2.144757	4.652237	-0.146451
H	3.684191	3.942115	-0.712721
H	1.283746	4.791227	-2.514384
H	2.754838	4.030047	-3.197019
H	1.142272	3.320428	-3.531804
H	1.370075	-4.482242	-0.027362
H	0.092785	-5.394076	1.923182
H	-2.197328	-4.526659	2.450645
H	-3.244801	-2.753124	1.077722
H	-2.463869	0.547012	-2.930128
H	-4.697306	1.327782	-3.701393
H	-6.795003	0.232416	-2.841456
H	-6.600551	-1.704281	-1.245203
H	-4.376727	-2.543158	-0.554806
H	-0.125238	0.756867	-1.439045

XRD Data

Experimental

Data Collection

A red prism crystal of $C_{39}H_{58}P_2Ru$ having approximate dimensions of 0.100 x 0.100 x 0.020 mm was mounted in a loop. All measurements were made on a Rigaku Saturn70 diffractometer using filtered Mo-Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 9.4786(4) Å
b = 19.3191(9) Å β = 100.019(7)^o
c = 19.159(2) Å
V = 3454.9(4) Å^3

For Z = 4 and F.W. = 689.90, the calculated density is 1.326 g/cm^3. The reflection conditions of:

h0l: h+l = 2n
0k0: k = 2n

uniquely determine the space group to be:

$P2_1/n$ (#14)

The data were collected at a temperature of -180 $\pm$ 1^{o}C to a maximum 2θ value of 50.7^o.

Data Reduction

Of the 34512 reflections that were collected, 6312 were unique (R_{int} = 0.0445); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).

The linear absorption coefficient, μ, for Mo-Kα radiation is 5.726 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.858 to 0.989. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms

were refined isotropically and the rest were refined using the riding model.The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 6312 observed reflections and 383 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0318$$

$$wR2 = [\Sigma \; (\; w \; (Fo^2 - Fc^2)^2 \;) / \; \Sigma \; w(Fo^2)^2]^{1/2} = 0.0765$$

The standard deviation of an observation of unit weight[4] was 0.95. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.74 and -0.53 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the CrystalStructure[9] crystallographic software package except for refinement, which was performed using SHELXL-97[10].

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

(3) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(10) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{39}H_{58}P_2Ru$
Formula Weight	689.90
Crystal Color, Habit	red, prism
Crystal Dimensions	0.100 X 0.100 X 0.020 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.4786(4) Å b = 19.3191(9) Å c = 19.159(2) Å β = 100.019(7) ° V = 3454.9(4) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.326 g/cm^3
F_{000}	1464.00
μ(MoKα)	5.726 cm^{-1}

B. Intensity Measurements

Diffractometer	Saturn70
Radiation	MoKα (λ = 0.71075 Å)
Voltage, Current	50kV, 16mA
Temperature	-180.0°C
Detector Aperture	71 x 71 mm
Pixel Size	0.070 mm
$2\theta_{max}$	50.7°
No. of Reflections Measured	Total: 34512 Unique: 6312 (R_{int} = 0.0445)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.858 - 0.989)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0352 \cdot P)^2 + 4.7356 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	50.7^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6312
No. Variables	383
Reflection/Parameter Ratio	16.48
Residuals: R1 (I>2.00σ(I))	0.0318
Residuals: R (All reflections)	0.0417
Residuals: wR2 (All reflections)	0.0765
Goodness of Fit Indicator	0.947
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	0.74 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.53 $e^-/Å^3$