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Formation of a Ruthenium μ-Carbide Complex with Acetylene as the Carbon Source

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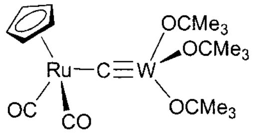
Reactions of the dinuclear ruthenium complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] with phenylacetylene or *tert*-butylacetylene gave the vinylidene complexes [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(=C=CHR)(PCy_3)] (R = *t*Bu, Ph), which were characterized crystallographically. With acetylene, however, a tetranuclear μ-carbide complex was obtained as evidenced by single-crystal X-ray analysis as well as by solid-state NMR spectroscopy. Experiments with fully ^{13}C-labelled acetylene showed that acetylene was the carbon source for the carbide ligand.

A complex containing a single carbon atom as a bridging ligand between a metalloporphyrin and a second metal-fragment was described for the first time in 1979.[1] Since then, several structurally related compounds with porphyrinato or phthalocyaninato ligands have been reported.[2] Well-characterized μ-carbide complexes without these ligands are still rare.[3] An early example was published by Latesky and Selegue in 1987.[3e] They showed that the reaction between [CpRu(C≡CMe)(CO)$_2$] and [W(≡CEt)(OCMe$_3$)$_3$] proceeds with elimination of 2-pentyne to give the heteronuclear μ-carbide complex [Cp(CO)$_2$Ru–C≡W(OCMe$_3$)$_3$] (**1**). More recently, it was observed that the terminal carbide complex [RuCl$_2$(≡C)(PCy$_3$)$_2$][4] can act as a 'σ-donor ligand' for other metals to form bimetallic complexes such as **2** and **3**.[3b] In the following, we describe a tetranuclear complex containing an unusual {Ru=C=Ru} unit. This complex was obtained by a novel reaction from acetylene by cleavage of the carbon triple bond.



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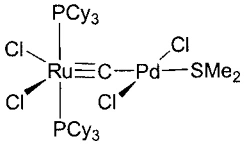

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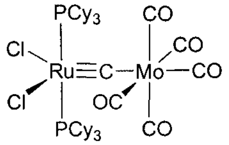

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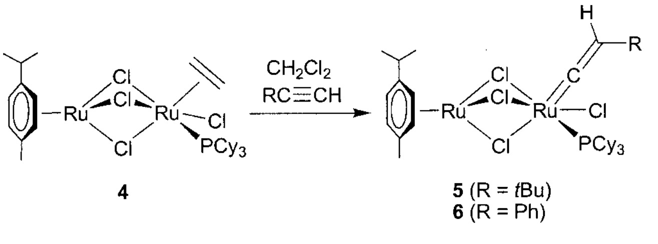
Over the last years, we investigated ruthenium complexes as catalysts for atom transfer radical reactions.[5] The halogeno-bridged complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy$_3$)] (**4**), which can easily be obtained from commercial [(*p*-cymene)RuCl$_2$]$_2$, was found to display an exceptionally high activity for atom transfer radical addition reactions under mild conditions.[5c] In order to further explore the reactivity of this complex, we have investigated the reaction of **4** with alkynes. When phenylacetylene or *tert*-butylacetylene was added to a solution of complex **4** in CH_2Cl_2 or benzene, the rapid and quantitative formation of a new complex was observed as evidenced by in situ ^{31}P NMR spectroscopic experiments (Scheme 1). The products **5** and **6** were isolated in nearly quantitative yields by evaporation of the solvent and washing with hexane.



Scheme 1.

Both complexes were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P; see Supporting Information), elemental analysis and single-crystal X-ray analysis (Figure 1 and Figure 2). The structures of **5** and **6** can be described as face-bridged dimers with a (*p*-cymene)Ru fragment con-

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nected by three chlorido bridges to a RuCl(=C=CHR)-(PCy_3) fragment.[6] The Ru1–C1 distances [1.817(6) Å for **5**; 1.778(8) Å for **6**] are comparable to those of other coordinatively saturated Ru–vinylidene complexes such as [TpRuCl-(=C=CHPh)(PPh_3)] [1.801(4) Å][7] or [{RuCl(*i*Pr_2-$PCH_2CH_2OMe)_2$(=C=CHPh)}(OTf)] [1.790(3) Å].[8] Apart from the vinylidene ligand, the bond lengths for **5** and **6** are similar to those for the starting material **4**. However, there is one notable exception: the Ru1–Cl1 bonds are significantly longer [2.6551(13) Å for **5**; 2.630(2) Å for **6**] than that of complex **4** [2.4878(6) Å]. This can be ascribed to the stronger *trans* influence of the vinylidene ligands relative to that of the ethylene ligand.

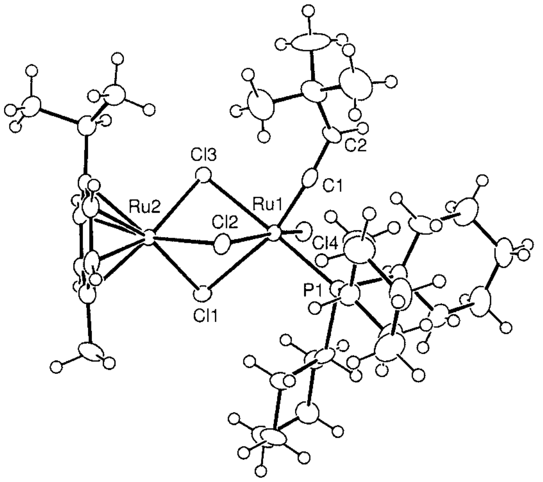


Figure 1. Graphical representation of the molecular structure of **5** in the crystal. The solvent molecules (CH_2Cl_2, 0.5 toluene) are not shown for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Cl1 2.6551(13), Ru1–Cl2 2.4221(14), Ru1–Cl3 2.5246(13), Ru1–Cl4 2.3672(14), Ru1–P1 2.3129(14), Ru1–C1 1.817(6), C1–C2 1.299(8), Ru2–Cl1 2.4376(15), Ru2–Cl2 2.4607(12), Ru2–Cl3 2.4397(13); Cl1–Ru1–C1 163.93(17), Cl4–Ru1–Cl2 165.61(5), Cl4–Ru1–P1 91.33(5).

The formation of **5** and **6** can be rationalized by the displacement of the ethylene ligand by the respective acetylene followed by an alkyne-to-vinylidene transformation.[9] A related reaction with a face-bridged Ru dimer was reported by Fogg et al., who found that the addition of *tert*-butylacetylene to [(dcypb)ClRu(μ-$Cl)_3$Ru(dcypb)(N_2)] {dcypb = 1,4-bis(dicyclohexylphosphanyl)butane} gave the vinylidene complex [(dcypb)ClRu(μ-$Cl)_3$Ru(=C=CH–*t*Bu)(dcypb)] by displacement of the dinitrogen ligand.[10]

When a solution of the olefin complex **4** in CH_2Cl_2 was treated with acetylene, the formation of a black product was observed, which was not characterized further. However, when a stoichiometric amount (1.2 equiv.) of acetylene was used in combination with thf as the solvent, a yellow-orange complex (**7**) precipitated.[11] Complex **7** displayed a very low solubility in all solvents. A detailed solution NMR analysis of **7** was therefore not possible, but crystals of sufficient quality for a single-crystal X-ray analysis were obtained from a dilute CH_2Cl_2 solution. Surprisingly, it was found that a tetranuclear μ-carbide complex had formed (Scheme 2 and Figure 3). The elemental analysis of **7** was in agreement with this result, and the total yield with respect to the starting material was 56%.

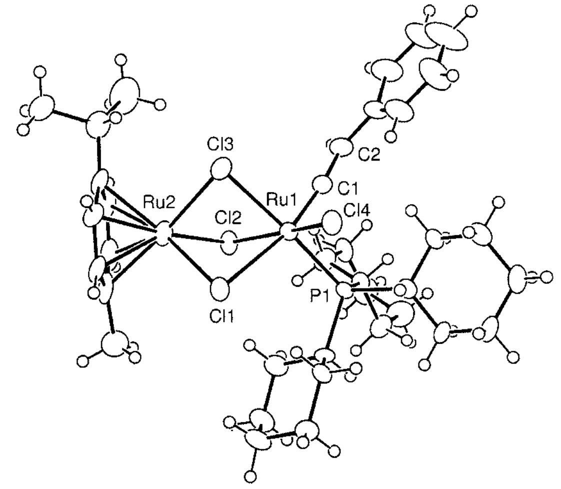
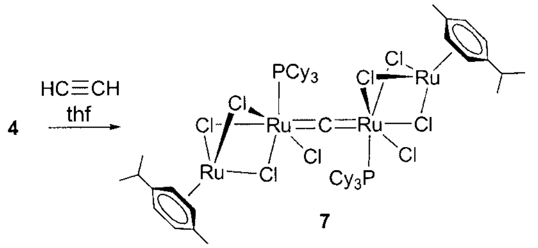


Figure 2. Graphical representation of the molecular structure of **6** in the crystal. The solvent molecules (2 toluene) are not shown for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Cl1 2.630(2), Ru1–Cl2 2.403(2), Ru1–Cl3 2.541(2), Ru1–Cl4 2.362(2), Ru1–P1 2.325(2), Ru1–C1 1.778(8), C1–C2 1.329(11), Ru2–Cl1 2.427(2), Ru2–Cl2 2.428(2), Ru2–Cl3 2.437(2); Cl1–Ru1–C1 167.0(3), Cl4–Ru1–Cl2 164.32(8), Cl4–Ru1–P1 92.76(8).



Scheme 2.

The molecular structure of complex **7** in the crystal consists of two symmetry-related[12] {(*p*-cymene)Ru(μ-$Cl)_3$-RuCl(PCy_3)} fragments connected by a carbide ligand in a nearly linear fashion [Ru1–C1–Ru1_2 = 178.8(9)°] (Figure 3). The Ru1–C1 bond length [1.7877(9) Å] is longer than that of the carbide complex **2** [1.662(2) Å][3b] and similar to the Ru–C distances found for the vinylidene complexes **5** and **6**. This confirms the {Ru=C=Ru} structure of complex **7** as depicted in Scheme 2. The octahedral geometry around Ru1 is highly distorted. Noteworthy is the long Ru1–Cl1 distance of 2.685(3) Å, which demonstrates that the μ-carbide ligand also has a very strong *trans* influence.

A priori, the carbon atom sandwiched between the two ruthenium atoms could have resulted from an acetylene-induced splitting of the ethylene ligand of complex **4** or from acetylene itself. To clarify this issue, the reaction was repeated with fully ^{13}C-labelled acetylene. The resulting product was investigated by solid-state MAS NMR spectroscopy. The $^{13}C\{^1H\}$ cross-polarized MAS NMR spectra of complex **7** show a strong signal at $\delta = 430.5$ ppm (Figure 4), which can clearly be attributed to the bridging car-

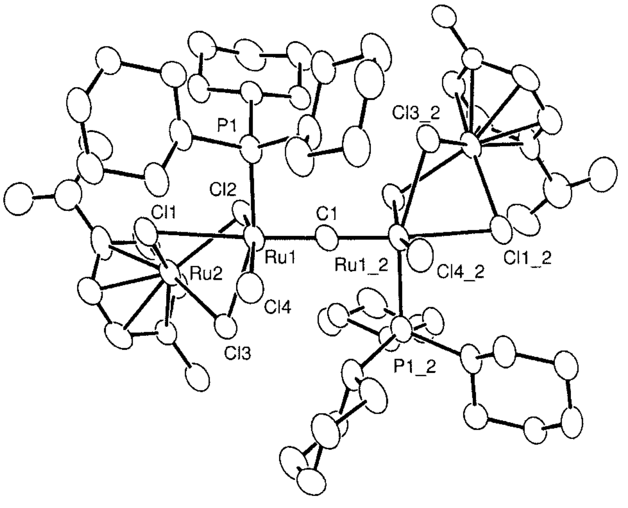


Figure 3. Graphical representation of the molecular structure of **7** in the crystal. The solvent molecules ($5\,CH_2Cl_2$) and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [°]: Ru1–C1 1.7877(9), Ru1–Cl1 2.685(3), Ru1–Cl2 2.439(3), Ru1–Cl3 2.548(3), Ru1–Cl4 2.365(3), Ru1–P1 2.350(4); Cl1–Ru1–C1 169.7(4), Cl4–Ru1–Cl2 162.99(11), Cl4–Ru1–P1 93.46(12), P1–Ru1–Cl3 161.75(11), Ru1–C1–Ru1_2 178.8(9).

bide ligand. The position of the signal is within the expected range as structurally related complexes such as **2** and **3** display resonances in the same region (**2**: δ = 381.2 ppm; **3**: δ = 446.3 ppm).[3b] These results demonstrate that the source of the μ-carbide ligand of complex **7** is indeed the acetylene.

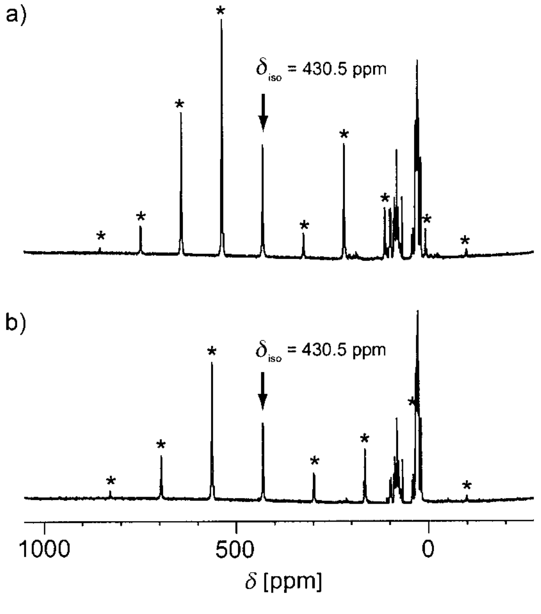


Figure 4. $^{13}C\{^1H\}$ cross-polarized (CP) MAS NMR spectra of solid complex **7** recorded at the spinning rates of (a) 8 kHz and (b) 10 kHz. The centreband, the isotropic chemical shift δ_{iso} = 430.5 ppm, of the C5 carbon resonance is indicated with an arrow, while the spinning sidebands are indicated by an *. The spectra are the result of averaging 12800 transients with a recycle interval of 3 s. The CP contact time was 5 ms.

In order to obtain information about possible side products of this unusual reaction, we investigated the mother liquor, from which complex **7** had precipitated, by solution NMR spectroscopy. The ^{31}P NMR spectrum shows several peaks with two dominant signals at δ = 61.82 and 66.00 ppm (see Supporting Information). The first signal appears as a doublet with a coupling constant of 17.9 Hz to a ^{13}C NMR signal at δ = 204.17 ppm. The second signal appears as a doublet of a doublet with a coupling constant of 20.2 Hz to a ^{13}C NMR signal at δ = 206.17 ppm and of 10.1 Hz to a ^{13}C signal at –10.46 ppm. The latter ^{13}C signal is assigned to a CH_3 group as evidenced by a ^{13}C NMR spectrum with coupling to ^1H. The high-field position of the signal suggests a Ru-bound methyl group. On the basis of this data we propose that the two major phosphane complexes in solution contain a $Ru(^{13}CX)(PCy_3)$ fragment (species at δ = 61.82 ppm) and a $Ru(^{13}CX)(^{13}CH_3)(PCy_3)$ fragment (species at δ = 66.00 ppm). The nature of the group/fragment 'X′ is currently not clear. From the chemical shift of the ^{13}C NMR signal at ca. 200 ppm, it can be excluded that X = Ru, and H-coupled spectra demonstrate that there are no protons directly bound to the ^{13}C carbon atom.

In summary, we have described the reaction of the dinuclear complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] (**4**) with alkynes. Whereas the vinylidene complexes **5** and **6** were obtained for phenylacetylene and *tert*-butylacetylene, the μ-carbide complex **7** was formed for reactions with acetylene. The latter represents a rare example of a structurally characterized Ru(μ-C)Ru complex. The available experimental data do not allow for the proposal of a mechanism for this unusual reaction. A plausible intermediate is the vinylidene complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C=CH_2)-(PCy_3)], which undergoes subsequent transformations. It should be noted that Ru(=C=CH_2) complexes are not intrinsically unstable as evidenced by the isolation of, for example, the complex [RuHCl(=C=CH_2)(P*t*Bu_2Me)$_2$].[13] The fact that complex **4** can promote the splitting of a carbon triple bond of acetylene at room temperature is further evidence for its high reactivity,[5c] and other organometallic transformations of this complex are currently being investigated in our laboratory.

Experimental Section

General: The synthesis of all complexes was performed under an atmosphere of dry argon by using standard Schlenk techniques. The complex [(*p*-cymene)Ru(μ-Cl)$_3$Ru(PCy_3)(C_2H_4)Cl] (**4**) was prepared as described before.[5c] The fully ^{13}C-labelled acetylene (99%) was obtained from Cambridge Isotope Laboratories, Inc. The ^1H- and ^{13}C NMR spectra in solution were recorded on Bruker Advance DPX 400, Advance 600 and Advance 800 instruments by using the residual protonated solvents as internal standards. Solid-state NMR spectra were recorded on a Bruker DRX 300 spectrometer equipped with a 7.0 widebore magnet and utilising a 4-mm CPMAS probehead. A nicely powdered sample was packed under a N_2 atmosphere into a 4-mm outer diameter ZrO_2 rotor. Chemical shifts of ^{13}C are reported in ppm relative to an external TMS standard.

Synthesis of Complex 5: [(*p*-cymene)Ru(μ-Cl)$_3$Ru(PCy$_3$)(C$_2$H$_4$)Cl] (**4**) (100 mg, 128 μmol) and *tert*-butylacetylene (19 μL, 154 μmol) in CH_2Cl_2 (5 mL) were stirred for 2 h under an inert atmosphere. After evaporation of the solvent under reduced pressure, the product was washed with hexane and dried under vacuum (isolated yield: 103 mg, 96%). Orange crystals were obtained from cold toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 9 H, *t*Bu), 1.20–1.32 (m, 9 H, PCy$_3$), 1.32 [d, ^3J = 7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.34 [d, ^3J = 7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.54–2.13 (m, 24 H, PCy$_3$), 2.30 (s, 3 H, CH$_3$), 2.96 [sept, ^3J = 7 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.83 (d, $^4J_{PH}$ = 3 Hz, 1 H, C*H*-*t*Bu), 5.37 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.50 (d, ^3J = 6 Hz, 1 H, CH, cymene), 5.58 (d, ^3J = 6 Hz, 1 H, CH, cymene) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.73 (CH$_3$, cymene), 22.07, 22.14 [CH(*C*H$_3$)$_2$, cymene], 26.32 (CH$_2$, PCy$_3$), 27.64 (d, $^3J_{PC}$ = 10 Hz, CH$_2$, PCy$_3$), 28.82 (d, $^2J_{PC}$ = 19 Hz, CH$_2$, PCy$_3$), 31.01 [*C*H(CH$_3$)$_2$, cymene], 33.13 (*t*Bu), 35.07 (d, $^1J_{PC}$ = 24 Hz, CH, PCy$_3$), 78.56, 78.78, 79.03, 79.78 (CH, cymene), 96.44, 101.19 (C, cymene), 122.23 (Ru=C=*C*), 352.55 (d, $^2J_{PC}$ = 19 Hz, Ru=C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 54.48 (s) ppm. $C_{34}H_{57}Cl_4PRu_2$ (840.74): calcd. C 48.57, H 6.83; found C 48.84, H 6.73.

Synthesis of Complex 6: The synthesis was performed analogously to that of complex **5** by using phenylacetylene (18 μL, 154 μmol) (isolated yield: 105 mg, 95%). Orange crystals were obtained from cold toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12–1.35 (m, 9 H, PCy$_3$), 1.34 [d, ^3J = 7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.36 [d, ^3J = 7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.52–2.17 (m, 24 H, PCy$_3$), 2.29 (s, 3 H, CH$_3$), 2.96 [sept, ^3J = 7 Hz, 1 H, C*H*(CH$_3$)$_2$], 4.91 [d, $^4J_{PH}$ = 4 Hz, 1 H, C*H*(Ph)], 5.41 (d, ^3J = 6 Hz, 2 H, CH, cymene), 5.55 (d, ^3J = 6 Hz, 1 H, CH, cymene), 5.64 (d, ^3J = 6 Hz, 1 H, CH, cymene), 6.88–7.14 (m, 5 H, Ph) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 18.80 (CH$_3$, cymene), 22.06, 22.35 [CH(*C*H$_3$)$_2$, cymene], 26.28 (CH$_2$, PCy$_3$), 27.69 (d, $^3J_{PC}$ = 11 Hz, CH$_2$, PCy$_3$), 28.89 (d, $^2J_{PC}$ = 15 Hz, CH$_2$, PCy$_3$), 31.16 [*C*H(CH$_3$)$_2$, cymene], 35.07 (d, $^1J_{PC}$ = 24 Hz, CH, PCy$_3$), 78.28, 78.79, 79.52, 80.04 (CH, cymene), 97.03, 101.12 (C, cymene), 114.10 (Ru=C=*C*), 124.42, 125.85, 128.06, 131.07 (Ph), 356.11 (d, $^2J_{PC}$ = 19 Hz, Ru=C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 54.21 (s) ppm. $C_{36}H_{53}Cl_4PRu_2$ (860.73): calcd. C 50.23, H 6.21; found C 50.14, H 6.24.

Synthesis of Complex 7: A fixed volume of acetylene (35 mL, 1.5 mmol) was connected to a 100-mL flask containing [(*p*-cymene)Ru(μ-Cl)$_3$Ru(PCy$_3$)(C$_2$H$_4$)Cl] (**4**) (1.00 g, 1.30 mmol) and thf (50 mL). The suspension was stirred for 24 h at room temperature during which the colour changed from orange-red to yellow-orange. The product was collected on a filter and dried in vacuo (yield: 560 mg, 56%). $C_{57}H_{94}Cl_8P_2Ru_4$ (1529.21): calcd. C 44.77, H 6.19; found C 44.65, H 6.11. Single crystals were obtained from CH_2Cl_2.

X-ray Analyses: Data collection was performed at 140(2) K with an Oxford Diffraction KM4 Sapphire CCD. Data reduction was carried out with CrysAlis RED, release 1.7.0.[14] Absorption correction was applied to both data sets. Structure solution and refinement were performed with the SHELXTL software package, release 5.1.[15] The structures were refined by using the full-matrix least-squares on F^2 with all non-H atoms anisotropically refined. H atoms were placed in calculated positions by using the 'riding model'. CCDC 624643–624645 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for Complex 5·CH$_2$Cl$_2$·0.5C$_6$H$_5$CH$_3$: $C_{38.5}H_{63}Cl_6PRu_2$, M = 971.70, triclinic, a = 10.3246(7), b = 13.0596(9), c = 17.2481(10) Å, α = 77.248(5), β = 85.836(5), γ = 73.173(6)°, V = 2171.1(2) Å^3, T = 140(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K_α) = 0.71073 Å, 13023 reflections collected, 6716 independent reflections, R_{int} = 0.0307, R_1 [$I > 2\sigma(I)$] = 0.0457, wR_2 (all data) = 0.1281.

Crystal Data for Complex 6·2C$_6$H$_5$CH$_3$: $C_{50}H_{69}Cl_4PRu_2$, M = 1044.96, monoclinic, a = 9.6774(4), b = 16.9682(9), c = 30.2874(17) Å, β = 97.243(4)°, V = 4933.7(4) Å^3, T = 140(2) K, space group $P2_1/c$, Z = 4, μ(Mo-K_α) = 0.71073 Å, 28793 reflections collected, 7990 independent reflections, R_{int} = 0.0587, R_1 [$I > 2\sigma(I)$] = 0.0648, wR_2 (all data) = 0.1549.

Crystal Data for Complex 7·5CH$_2$Cl$_2$: $C_{62}H_{104}Cl_{18}P_2Ru_4$, M = 1953.77, monoclinic, a = 17.8078(15), b = 23.903(3), c = 18.5150(17) Å, β = 91.104(7)°, V = 7879.7(13) Å^3, T = 140(2) K, space group $C2/c$, Z = 4, μ(Mo-K_α) = 0.71073 Å, 22389 reflections collected, 6566 independent reflections, R_{int} = 0.1115, R_1 [$I > 2\sigma(I)$] = 0.0905, wR_2 (all data) = 0.2645.

Supporting Information (see footnote on the first page of this article): ^{13}C- and ^{31}P NMR spectra of the mother liquor of the reaction between complex **4** and fully ^{13}C-labelled acetylene.

Acknowledgments

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[1] I. Noda, S. Kato, M. Mizuta, N. Yasuoka, N. Kasai, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 83.

[2] For selected examples see: a) L. Galich, A. Kienast, H. Hückstädt, H. Homborg, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1235–1242; b) A. Kienast, L. Galich, K. S. Murray, B. Moubaraki, G. Lazerev, J. D. Cashion, H. Homborg, *J. Porph. Phthalocyan.* **1997**, *1*, 141–157; c) A. M. Paoletti, G. Pennesi, C. Ercolani, *Inorg. Chem.* **1995**, *34*, 4780–4784; d) W. Beck, W. Knauer, C. Robl, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 318–320; e) C. Ercolani, M. Gardini, V. L. Goedken, G. Pennesi, G. Rossi, U. Russo, P. Zanonato, *Inorg. Chem.* **1989**, *28*, 3097–3099; f) D. Mansuy, J.-P. Lecomte, J.-C. Chottard, J.-F. Bartoli, *Inorg. Chem.* **1981**, *20*, 3119–3121.

[3] a) S. H. Hong, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, *126*, 7414–7415; b) A. Hejl, T. M. Trnka, M. W. Day, R. H. Grubbs, *Chem. Commun.* **2002**, 2524–2525; c) R. L. Miller, P. T. Wolczanski, *J. Am. Chem. Soc.* **1993**, *115*, 10422–10423; d) M. Etienne, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1991**, *113*, 2324–2325; e) S. L. Latesky, J. P. Selegue, *J. Am. Chem. Soc.* **1987**, *109*, 4731–4733.

[4] a) S. R. Caskey, M. H. Stewart, J. E. Kivela, J. R. Sootsman, M. J. A. Johnson, J. W. Kampf, *J. Am. Chem. Soc.* **2005**, *127*, 16750–16751; b) R. G. Carlson, M. A. Gile, J. A. Heppert, M. H. Mason, D. R. Powell, D. V. Velde, J. M. Vilain, *J. Am. Chem. Soc.* **2002**, *124*, 1580–1581.

[5] a) L. Quebatte, K. Thommes, K. Severin, *J. Am. Chem. Soc.* **2006**, *128*, 7440–7441; b) M. Haas, E. Solari, Q. T. Nguyen, S. Gauthier, R. Scopelliti, K. Severin, *Adv. Synth. Catal.* **2006**, *348*, 439–442; c) L. Quebatte, E. Solari, R. Scopelliti, K. Severin, *Organometallics* **2005**, *24*, 1404–1406; d) L. Quebatte, M. Haas, E. Solari, R. Scopelliti, Q. T. Nguyen, K. Severin, *Angew. Chem. Int. Ed.* **2005**, *44*, 1084–1088; e) L. Quebatte, R. Scopelliti, K. Severin, *Eur. J. Inorg. Chem.* **2005**, 3353–3358; f) L. Quebatte, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2004**, *43*, 1520–1524.

[6] For Ru(μ-Cl)$_3$Ru complexes containing (arene)Ru and (PR$_3$) Ru fragments see: a) S. Gauthier, L. Quebatte, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2004**, *10*, 2811–2821; b) M. P. de Araujo, E. M. A. Valle, J. Ellena, E. E. Castellano, E. N. dos Santos,

A. A. Batista, *Polyhedron* **2004**, *23*, 3163–3172; c) A. C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, *Eur. J. Inorg. Chem.* **2001**, 685–691.

[7] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, *Organometallics* **1996**, *15*, 5275–5277.

[8] M. Martin, O. Gevert, H. Werner, *J. Chem. Soc., Dalton Trans.* **1996**, 2275–2283.

[9] For a recent discussion of this transformation see: D. B. Grotjahn, X. Zeng, A. L. Cooksy, *J. Am. Chem. Soc.* **2006**, *128*, 2798–2799.

[10] D. Amoroso, G. P. A. Yap, D. E. Fogg, *Organometallics* **2002**, *21*, 3335–3343.

[11] Contrary to that which had been observed for reactions in CH_2Cl_2, a larger excess of acetylene (18 equiv.) also resulted in the formation of complex **7**. The yield was similar to that of reactions with equimolar amounts of acetylene, but the purity was slightly lower as evidenced by solid-state ^{31}P NMR spectroscopy.

[12] The symmetry operation is: $-x$, y, $-z+1/2$.

[13] M. Oliván, E. Clot, O. Eisenstein, K. G. Caulton, *Organometallics* **1998**, *17*, 897–901.

[14] Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, **2003**.

[15] G. M. Sheldrick, University of Göttingen, Germany, **1997**; Bruker AXS, Inc., Madison, Wisconsin, 53719, USA, **1997**.

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