

The Aza-Cope Rearrangement in Transition Metal Complexes. Construction of an Unsaturated C₇-Ligand from Butadiyne and an Allylic Amine

Rainer F. Winter* and Fridmann M. Hornung

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany

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Summary: *cis*-RuCl₂(L₂)₂ reacts with butadiyne in the presence of NaPF₆ to give the butatrienylidene intermediate *trans*-[RuCl(L₂)₂=C=C=C=CH₂]⁺, which can be trapped with tertiary amines to afford the ammonio-butenynyl complexes *trans*-[RuCl(L₂)₂-C≡C-C(NR₃)=CH₂]⁺ (L₂ = *dppm*; R = Et, Pr). The respective *N*-allyl derivatives *trans*-[RuCl(L₂)₂-C≡C-C((NMe₂)allyl)=CH₂]⁺ (L = *dppm*, *depe*) rearrange under ambient conditions via an aza-Cope process to the amino-substituted allenylidene complexes *trans*-[RuCl(L₂)₂=C=C=C(NMe₂)(CH₂)₂CH=CH₂]⁺.

Coordinatively stabilized C_n ligands of higher chain lengths built exclusively from sp-hybridized carbon atoms are not only appealing synthetic goals but also interesting materials with unusual physical and material properties. They serve as model compounds for “molecular wires”¹ or high-spin materials,² and some representatives have been found to exhibit nonlinear optical³ or liquid crystalline properties.⁴ Within this context, alkynyl- and alkenylidene ligands have to be distinguished. Allenylidene⁵ and pentatetraenylidene complexes⁶ are the first members of the latter family with an odd number of carbon atoms within the unsaturated chain. Reports about corresponding systems with an even number of carbon atoms are still quite scarce and restricted to the butatrienylidene ligand.^{7,8} While this work was in progress, Bruce et al. showed

this ligand to regioselectively add phosphorus nucleophiles,^{7b} to add protic nucleophiles to the terminal C=C bond leading to functionalized allenylidene complexes, or to engage in cycloaddition reactions with aromatic imines.^{7c} Coordinatively unsaturated 16 valence electron ruthenium cations are able to isomerize terminal alkynes RC≡CH to cationic vinylidene complexes [Ru]=C=CHR]⁺. These are the conjugate acids of neutral alkynyl complexes [Ru]-C≡CR], and many cases are known where such transformations have successfully been performed in the presence of a base.^{3b,5a,9} Substitution of the simple alkynes RC≡CH for diynes RC≡C-C≡CH is thus expected to give diyne compounds [Ru]-C≡C-C≡CR via butatrienylidene intermediates [Ru]=C=C=C=CHR]⁺. An appropriate choice of R should render these diyne complexes valuable starting materials for the construction of C₄ or C₈ bridged dimetal compounds,^{1b,10} which deserve special attention for their unusual electronic properties. For this purpose, butadiyne (R = H) should be an ideal starting material.

In our initial studies, we chose [ClRu(*dppm*)₂]⁺ (**1a**, *dppm* = bis(diphenylphosphino)methane) as the ruthenium complex fragment. The latter species is generated *in situ* from the corresponding *cis*-dichloro compound in the presence of NaPF₆. When KO^tBu or DBU was added to the dark green solutions obtained after treating **1a** with excess butadiyne in dichloromethane or THF, complex product mixtures were produced from which no pure materials could be isolated.

The tertiary amines NEt₃ and NPr₃, however, were found to selectively add to the electrophilic C_γ atom of the proposed butatrienylidene intermediate **2a** (see Scheme 1). After chromatographic workup, the ammonio-butenynyl adducts *trans*-[RuCl(*dppm*)₂-C≡C-C(NR₃)=CH₂]⁺PF₆⁻ (**3a**, R = Et; **3b**, R = Pr) were isolated

* To whom correspondence should be addressed. Fax: +49 711 685 4165. E-mail: winter@anorg55.chemie.uni-stuttgart.de.

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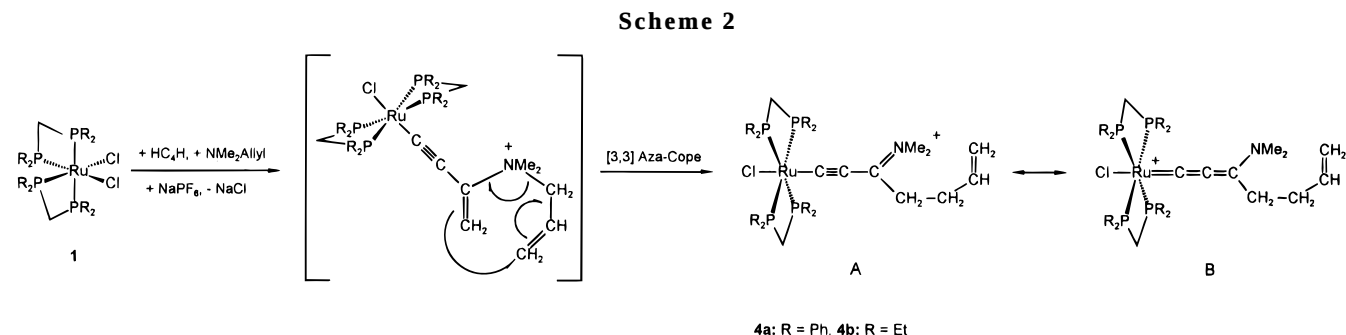
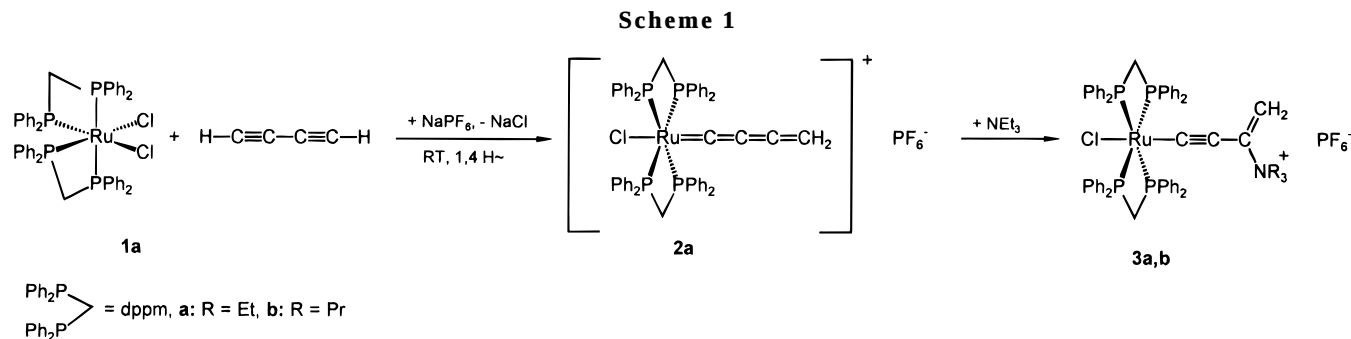
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as bluish green or dark green microcrystalline solids and characterized by IR, UV/vis, ^1H , ^{13}C , and ^{31}P NMR spectroscopy¹¹ and, in the case of **3a**, by an X-ray structure analysis.¹² The most important spectroscopic features in the proton NMR spectra are the two separate doublet signals of the vinyl protons with a small geminal coupling constant of about 3 Hz and the two components of an ABXX'YY' spin system due to the methylene protons of the dpmp ligand. In the ^1H NMR spectra, the resonance signals of the corresponding amines are found with an integral ratio confirming the proposed product

(11) **3a**: yield 58%. Selected characterization data: ^1H NMR (250.133 MHz, CDCl_3 , 300 K) δ 0.65 (t, NCH_2CH_3 , 9H, $^2J_{\text{H-H}} = 7.15$ Hz), 2.46 (q, NCH_2 , 6H, $^3J_{\text{H-H}} = 7.15$ Hz), 3.80 (d, $\text{C}=\text{CHH}$, 1H, $^2J_{\text{H-H}} = 3.04$ Hz), 4.60 (d, $\text{C}=\text{CHH}$, 1H, $^2J_{\text{H-H}} = 3.04$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3 , 300 K) δ 7.87 (NCH_2CH_3), 51.83 (NCH_2), 53.82 (C2), 100.04 (br, C3), 111.35 (C4), 146.22 (quint, C1, $J_{\text{P-C}} = 14.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3 , 300 K, $\text{H}_3\text{PO}_4(\text{ext.})$) δ -5.8 (s, P(dppm)); IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2032 (cm^{-1}). Anal. Calcd for $\text{C}_{60}\text{H}_{61}\text{ClF}_6\text{NP}_5\text{Ru}$: C, 59.98; H, 5.12; N, 1.17. Found: C, 59.55; H, 5.25; N, 1.26. **3b**: yield 56%. Selected characterization data: ^1H NMR (250.1 MHz, CDCl_3 , 300 K) δ 0.70 (t, CH_3 (Pr), 9H, $^3J_{\text{H-H}} = 7.14$ Hz), 1.14 (m, CH_2 (Pr), 6H), 2.47 (m, NCH_2 , 6H), 4.12 (d, $\text{C}=\text{CHH}$, 1H, $^2J_{\text{H-H}} = 2.88$ Hz), 4.68 (d, $\text{C}=\text{CHH}$, 1H, $^2J_{\text{H-H}} = 2.88$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3 , 300 K) δ 11.02 (CH_3), 15.42 (CH_2 (Pr)), 53.77 (C2), 59.31 (NCH_2), 103.70 (br, C3), 110.17 (C4), 146.03 (quint, C1, $J_{\text{P-C}} = 14.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3 , 300 K, $\text{H}_3\text{PO}_4(\text{ext.})$) δ -4.1 (s, P(dppm)); IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2027 (cm^{-1}). Anal. Calcd for $\text{C}_{63}\text{H}_{67}\text{ClF}_6\text{NP}_5\text{Ru}$: C, 60.85; H, 5.43; N, 1.13. Found: C, 60.57; H, 5.24; N, 1.12.

(12) Crystal data for **3a**: [C₆₀H₆₁NCIP₄Ru][PF₆], *M_r* = 1202.48, blue-green crystal obtained from CH₂Cl₂ at ambient temperature; monoclinic, space group *P2₁/n*, *a* = 13.167(3), *b* = 21.127(4), and *c* = 20.644(4) Å, *β* = 96.94(3)°, *V* = 5701(2) Å³, *Z* = 4, *D*_{calcd} = 1.401 g cm⁻³, *T* = 183(2) K, *μ*(Mo Kα) = 0.521 mm⁻¹, *F*(000) = 2476, Siemens four-circle diffractometer P4, graphite-monochromated Mo Kα radiation (*λ* = 0.710 73 Å); 9685 reflections measured (3.48 ≤ 2*θ* ≤ 26°), 7910 independent, 7698 observed, 618 parameters. The structure was solved by direct methods and refined on *F*² (SHELXL93).¹³ Besides two carbon atoms, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at their geometric positions and treated according to the riding model. Final *R*1 = 0.1832 (*I* > 2σ(*I*)) and *wR*2 = 0.4194 (all data), GOF = 3.932; the maximum and minimum peaks in the final difference Fourier map corresponded to -2.199/1.504 e Å⁻³. The constitution of the complex cation could unequivocally be determined. The relatively high *R* and GOF values arise from cocrystallized CH₂Cl₂, which could not be localized or considered as disordered or partially occupied. The packing diagram reveals tubular channels formed by the hydrophobic phenyl rings of the dppm ligands. We assume that the solvent resides in these channels.

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composition. All four resonance signals of the unsaturated ligand are identified in the ^{13}C NMR spectra.¹¹ A plot of the crystallographically determined structure of **3a** is shown in Figure 1, along with the most important bond lengths and angles. The C_4N ligand is essentially planar, with the Ru and the Cl atoms residing in the same plane, which forms an interplanar angle of $87.3\text{--}(4)^\circ$ to the best plane, RuP_4 . Although the low quality of this structure does not provide a firm basis for a detailed discussion of individual bond parameters, the Ru–C and the C–C bond lengths and angles within the unsaturated ligand follow the proposed bonding scheme. Tertiary amines that are not too sterically demanding thus behave as nucleophiles rather than as bases toward the butatrienylidene intermediate **2a**. We note that a phosphonio derivative related to **3a,b** has already been communicated by Bruce et al.^{7b} As in their case and in the case of other authors,^{7a} all our attempts to produce

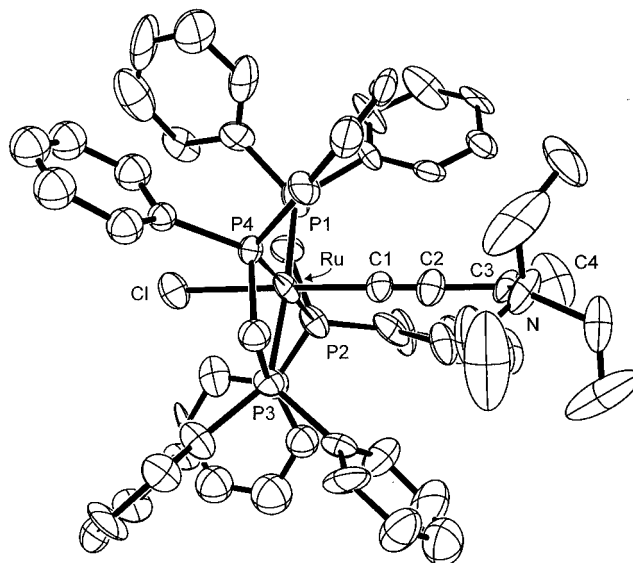


Figure 1. ORTEP plot of the cation of **3a**. Selected bond distances (Å) and angles (deg): Ru–C1 2.02(2), C1–C2 1.12(2), C2–C3 1.51(2), C3–C4 1.34(3), C3–N 1.47(2), Ru–C1–C2 175(2), C1–C2–C3 167(2), C2–C3–C4 124(2), C2–C3–N 113(2), N–C3–C4 123(2).

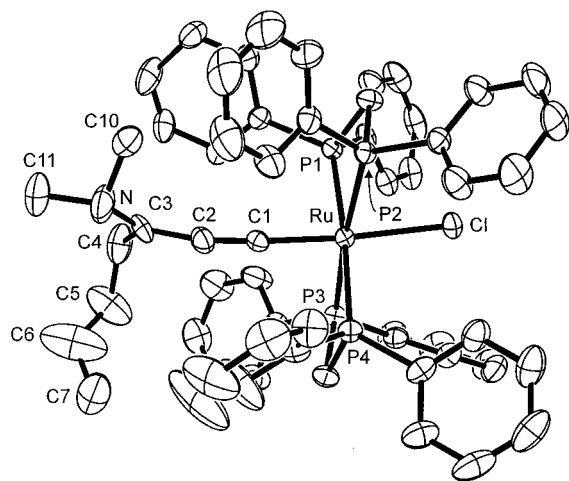


Figure 2. ORTEP plot of the cation of **4a**. The PF_6^- counterion and the solvent molecules are omitted for clarity (only one of the two disordered cations is shown). Selected bond distances (Å) and angles (deg): Ru–C1 1.950(4), C1–C2 1.218(6), C2–C3 1.372(9), C3–N 1.244(8), C3–C4 1.496(8), N–C10 1.505(7), N–C11 1.495(6), Ru–C1–C2 175.3(4), C1–C2–C3 175.1(6).

further evidence for the proposed butatrienylidene intermediate $[\{\text{Ru}\}=\text{C}=\text{C}=\text{C}=\text{CH}_2]^+$ were unsuccessful. Nevertheless, the formation of **3a,b** is in complete agreement with such an intermediate.

We were now interested in studying whether this reaction type tolerates an unsaturated functionality in the amine side chain as is present in $(\text{NMe}_2)\text{allyl}$ and obtained an unexpected result: The primary adduct, a quaternary allyleneammonium salt, rearranges at room temperature to the dimethylamino-substituted allenylidene complex **4a** with a γ,δ unsaturated side chain (see Scheme 2).¹⁴ The depe derivative **2b** (depe = bis-(diethylphosphino)ethane) reacts analogously to give **4b**.¹⁵ Spectroscopic characteristics of the rearranged products are the strong bands at 1995 cm^{-1} (**4a**) or 1979 cm^{-1} (**4b**), the low-field quintet signal of the α carbon of the allenylidene ligand in the ^{13}C NMR spectra, and the two sets of methylene signals in the aliphatic region. The methyl substituents on nitrogen give rise to two separate resonance signals indicating a hindered rotation around the C3–N bond.¹⁶ Figure 2 gives a representation of the crystallographically determined structure of **4a**, together with pertinent bond lengths and angles.²⁰ As is evident from Figure 2, the formerly N-bound allyl substituent has been transferred to C₄ of the former

butenynyl ligand. The almost linear Ru–allene unit exhibits a significant bond length alternation. In accordance with the iminoalkynyl resonance form B (Scheme 2), the distance C1–C2 (1.218(6) Å) is typical of a $\text{C}\equiv\text{C}$ triple bond, and the bond length C2–C3 of 1.372(9) Å resembles a single bond between sp-hybridized C atoms rather than a $\text{C}=\text{C}$ double bond. Similar trends have been observed in neutral allenylidene complexes of the pentacarbonylchromium or -tungsten fragment (C1–C2 = 1.204–1.236 Å, C2–C3 = 1.372–1.399 Å).^{16b,17–19} In addition, we find that the C3–N bond in **4a** is considerably shorter than the N-methyl bonds.

To the best of our knowledge, the formation of **4a,b** represents the first examples for an aza-Cope rearrangement within the coordination sphere of a transition metal complex. It is interesting to note that the primary adducts rearrange to **4a,b** under ambient conditions, while comparable metal-free quaternary alkylated ene-ammonium salts mostly require temperatures of about $80\text{ }^\circ\text{C}$.²¹ Tertiary metal-substituted eneamines, however, are seemingly inert under these conditions.¹⁶ One further novelty arises from the fact that, unlike all other cases, the vinyl function and not an allyl or alkyl group is introduced in the quaternization step.

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Supporting Information Available: Text giving detailed information on the synthesis of **3a,b** and **4a,b** and a full account of spectroscopic data, tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles and anisotropic displacement parameters for **3a** and **4a**, and packing diagrams for both structures, one diagram showing the hydrophobic tubes within the structure of **3a** (29 pages). Ordering information is given on any current masthead page.

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(20) Crystal data for **4a**: $[\text{C}_{59}\text{H}_{57}\text{NClP}_4\text{Ru}][\text{PF}_6] \cdot 1.5\text{CH}_2\text{Cl}_2$, $M_r = 1312.82$; green crystals were obtained by layering a concentrated solution in CH_2Cl_2 with Et_2O at $4\text{ }^\circ\text{C}$; triclinic, $P1$, $a = 12.3221(12)$, $b = 15.9456(9)$, and $c = 15.9570(10)$ Å, $\alpha = 88.583(6)$, $\beta = 89.083(6)$, and $\gamma = 70.890(7)^\circ$, $V = 2961.5(4)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.472\text{ g cm}^{-3}$, $T = 183(2)\text{ K}$, $\mu(\text{Mo K}\alpha) = 0.685\text{ mm}^{-1}$, $F(000) = 1342$, Siemens four-circle diffractometer P4, graphite-monochromated Mo K α ($\lambda = 0.71073$ Å); 13 440 reflections in the range $3.5 \leq 2\theta \leq 54^\circ$, 12 828 independent; 12 249 observed reflections were used to refine 804 parameters with 39 constraints; $R1 = 0.0579$ ($I > 2\sigma(I)$), $wR2 = 0.1731$ (all data), $\text{GOF} = 1.076$, minimum and maximum peak of residual electron density in the final Fourier map $-0.871/1.072\text{ e } \text{\AA}^{-3}$. The structure was solved by direct methods (SHELXTL-Plus) and refined on F^2 (SHELXL93). With the exception of the solvent carbon atoms, all non-H atoms were refined with anisotropic thermal parameters. One phenyl ring (ratio 0.501(0.009)/0.499(0.009)), C10 (0.54(0.02)/0.46(0.02)), C3x, C4–C7 (0.578(0.009)/0.422(0.009)) of the carbon chain and one solvent molecule (0.75(0.02)/0.25(0.02)) were found to be disordered; an additional solvent molecule was refined as “half-occupied”. All hydrogen atoms were introduced at their geometric positions and treated according to the “riding model”. Atomic coordinates, bond lengths and angles, and thermal parameters of **3a** and **4a** have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EZ, UK (deposition no. CCDC-100-155).

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(14) Yield: 51%. Selected characterization data: ^1H NMR (250.133 MHz, CDCl_3 , 300 K) δ 1.35 (m, CH_2 (butenyl), 2H), 1.52 (m, CH_2 (butenyl), 2H), 2.02 (s, NCH_3 , 3H), 2.82 (s, NCH_3 , 3H), 4.77 (dd, $\text{trans HC}=\text{CHH}$, $^2J_{\text{H-H}} = 1.36\text{ Hz}$, $^3J_{\text{H-H}} = 16.95\text{ Hz}$, 1H), 4.92 (dd, $\text{cis-HC}=\text{CHH}$, $^2J_{\text{H-H}} = 1.36\text{ Hz}$, $^3J_{\text{H-H}} = 10.24\text{ Hz}$, 1H), 5.34 (m, $\text{HC}=\text{CH}_2$, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3 , 300 K) δ 28.89 (CH_2 (butenyl)), 35.51 (CH_2 (butenyl)), 40.40 (CH_3N), 43.16 (CH_3N), 116.18 ($\text{C}=\text{CH}_2$ (butenyl)), 118.73 (C2), 135.22 ($\text{C}=\text{CH}_2$ (butenyl)), 156.91 (C3), 202.09 (quint, C1, $J_{\text{P-C}} = 13.9\text{ Hz}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3 , 300 K, $\text{H}_3\text{PO}_4(\text{ext.})$) δ -8.2 (s, P(ppm)); IR (KBr) $\nu(\text{C}=\text{C})$ 1995 (s) cm^{-1} . Anal. Calcd for $\text{C}_{59}\text{H}_{57}\text{ClF}_6\text{NP}_4\text{Ru}$: C, 59.78; H, 4.84; N, 1.18. Found: C, 59.05; H, 4.82; N, 1.21.

(15) **4b**: yield 35%. Selected characterization data for **4b**: ^1H NMR (250.133 MHz, CDCl_3 , 300 K) δ 2.28 (m, CH_2 (butenyl), 2H), 2.51 (m, CH_2 (butenyl), 2H), 3.18 (s, NCH_3 , 3H), 3.28 (s, NCH_3 , 3H), 5.01 (dd, $\text{trans-HC}=\text{CHH}$, $^2J_{\text{H-H}} = 1.32\text{ Hz}$, $^3J_{\text{H-H}} = 18.9\text{ Hz}$, 1H), 5.02 (dd, $\text{cis-HC}=\text{CHH}$, $^2J_{\text{H-H}} = 1.32\text{ Hz}$, $^3J_{\text{H-H}} = 12.50\text{ Hz}$, 1H), 5.75 (m, $\text{HC}=\text{CH}_2$ (butenyl), 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, CDCl_3 , 300 K) δ 30.86 (CH_2 (butenyl)), 37.42 (CH_2 (butenyl)), 40.74 (NCH_3), 44.39 (NCH_3), 116.49 ($\text{HC}=\text{CH}_2$), 117.89 (C2), 135.28 ($\text{HC}=\text{CH}_2$), 155.40 (C3), 211.09 (quint, C1, $J_{\text{P-C}} = 13.7\text{ Hz}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (101.3 MHz, CDCl_3 , 300 K, $\text{H}_3\text{PO}_4(\text{ext.})$) δ 47.58 (s, P(depe)); IR (KBr) $\nu(\text{C}=\text{C})$ 1979 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{61}\text{ClF}_6\text{NP}_5\text{Ru} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 40.65; H, 7.17; N, 1.61. Found: C, 40.84; H, 6.94; N, 1.59.