Unsaturated Carbenes

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Synthesis of Allenylidene Lithium and Silver Complexes, and Subsequent Transmetalation Reactions**

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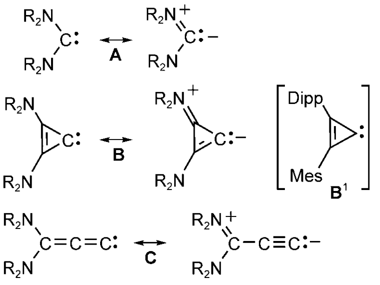
Since the discovery of the first stable singlet carbenes,[1,2] the stabilizing role of π-donating substituents, directly bonded to the electron-deficient center (as in **A**; Scheme 1), have been well established.[3] More recently, it has been shown that bis(diisopropylamino)cyclopropenylidene (**B**; R = *i*Pr) could also be isolated,[4,5] whereas **B^1**, which bears very bulky aryl substituents, dimerizes to give the corresponding triafulvalene.[6] These results clearly indicate that amino groups in the β position, provided they are conjugated, can also stabilize electron-deficient centers. This led us to consider if one of the isomers of cyclopropenylidenes **B**, namely propadienylidenes **C**,[7] could similarly be stabilized by amino groups. Although in this case the π donors are in γ positions, they can interact with the carbene center through the adjacent CC π system, just as in **B**. Note that the parent free allenylidene $H_2C{=}C{=}C$ has been observed spectroscopically in several hydrocarbon-rich flames and may be involved in the chemistry of soot formation.[8]



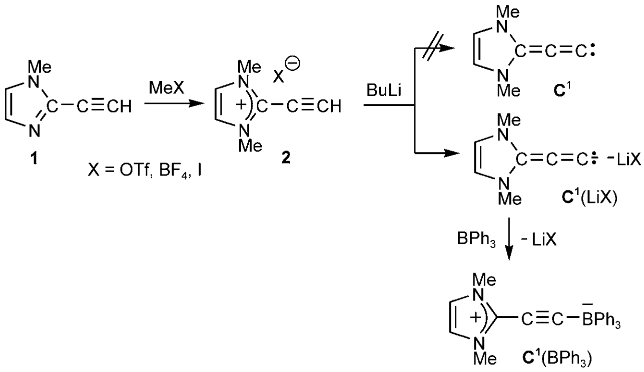
Scheme 1. Stabilizing effect of amino groups on singlet carbenes **A**, cyclopropenylidenes **B**, and propadienylidenes **C**.

Although no free allenylidenes have been isolated, allenylidene complexes, first prepared in 1976,[9] have been extensively studied.[10,11] They have found applications in stoichiometric organic synthesis,[12] catalysis,[13] and materials science.[14] They are generally generated in the coordination sphere of the metal, often using propargylic alcohols as sources of the allenylidene C_3 fragment, a strategy introduced by Selegue.[15] In 2006, Fischer and co-workers reported the first example of allenylidene transfer from chromium to tungsten,[16] but later stated that this exchange process could not be extrapolated to other metals, such as palladium.[17]

Herein we report our attempts to isolate a free (diamino)allenylidene **C**, which resulted in the characterization of the first allenylidene lithium adduct. Moreover, we describe the synthesis of a silver complex and subsequent transmetalation reactions with palladium and ruthenium.

To maximize the π donation, we chose a cyclic, unsaturated, diamino fragment.[18] 2-Ethynyl-1-methylimidazole (**1**) was synthesized in three steps according to published procedures.[19] Subsequent reaction with a variety of methylating reagents (MeOTf, Me_3OBF_4, and MeI; Tf = trifluoromethanesulfonyl) led to the desired imidazolium salts **2**, which were isolated in low yields as dark brown crystals (Scheme 2). Salts **2** were fully characterized by NMR spectroscopy, and **2** ($X = I^-$) was subjected to single-crystal X-ray diffraction analysis.[20] Computational studies at the RI-BP86/TZVP level of theory,[21] shows the corresponding allenylidene **C^1** to be a minimum on the energy hypersurface.[22] As expected, compared to the experimentally observed geometry of the protonated precursor **2** (Figure 1, left), the optimized geometry of the allenylidene **C^1** (Figure 1, right), shows that the $C\alpha{-}C\beta$ and $C\beta{-}C\gamma$ bonds are longer (1.26 versus 1.18(2) Å) and shorter (1.37 versus 1.42(2) Å), respectively. Interestingly, the frontier orbitals refer to those of a singlet carbene; the HOMO and LUMO are a σ lone pair and a p orbital, respectively.[21]

The singlet–triplet gap for **C^1** was calculated to be 60.5 kcal mol^{-1}, which is smaller than that of the parent unsaturated N-heterocyclic carbene (NHC) (79–84 kcal



Scheme 2. Synthesis of allenylidene lithium **C^1**(LiX) and borane **C^1**(BPh_3) adducts.

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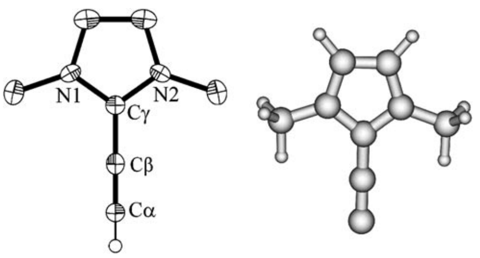

Figure 1. X-ray crystal structure of **2** (X = I$^-$; left) and optimized geometry of **C**^{1} (right). Hydrogen atoms and I$^-$ counterion in **2** (X = I$^-$) are omitted for clarity. Selected bond lengths [Å] and angles [°]. **2** (X = I$^-$): Cα–Cβ 1.18(2), Cβ–Cγ 1.420(19), Cγ–N1 1.339(11), Cγ–N2 1.339(11); N1-Cγ-N2 109.1(11) Cα-Cβ-Cγ 180.000(9). **C**^{1}: Cα–Cβ 1.263, Cβ–Cγ 1.379, Cγ–N1 1.380, Cγ–N2 1.380; N1-Cγ-N2 105.4, Cα-Cβ-Cγ 180.0.

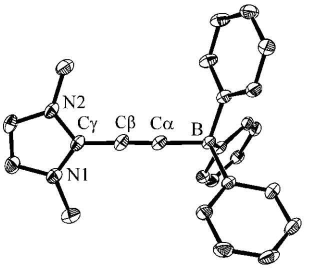

Figure 2. X-ray crystal structure of **C**^{1}(BPh$_3$). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cα–B 1.5960(16), Cα–Cβ 1.2168(16), Cβ–Cγ 1.4011(16), Cγ–N1 1.3501(14), Cγ–N2 1.3410(16); N1-Cγ-N2 107.55(10); B1-Cα-Cβ 178.49(11), Cα-Cβ-Cγ 177.54(13).

mol^{-1}),[23] but comparable to the parent diaminocyclopropenylidene **B** (R = H) (59.5 kcal mol^{-1}).[4] This was an encouraging indicator that **C**^{1} may be sufficiently stable to be isolated.

Deprotonation of triflate salt **2** (X = OTf) with *n*BuLi in THF led to a darkly colored solution. The ^{1}H NMR spectrum confirmed the deprotonation and revealed only two signals attributable to a symmetrical dimethylimidazole moiety. The ^{13}C NMR spectrum also clearly showed the loss of the alkynyl proton, and three new signals at $\delta = 90.6$, 133.6, and 190.2 ppm, corresponding to quaternary carbon nuclei. Although the calculated chemical shifts for the Cβ and Cγ atoms of free allenylidene **C**^{1} ($\delta = 99.8$ and 123.5 ppm, respectively) fit reasonably well with the observed signals, that of the terminal carbon atom Cα differs by nearly 100 ppm ($\delta = 285$ ppm). Additionally, despite several washings of the solid, a quartet centered at $\delta = 121$ ppm ($^1J_{CF} = 320$ Hz), typical for a triflate counterion, was apparent. Lastly, ^{7}Li NMR spectroscopy demonstrated the presence of lithium ($\delta = 0.66$ ppm), and therefore it can be concluded that deprotonation does not lead to the free allenylidene **C**^{1}, but to the lithium triflate adduct **C**^{1}(LiOTf). It is interesting to note that both the lithium adducts[24] and the free species[4] have been isolated for cyclopropenylidene **B**, as well as for various diaminocarbenes.[25] However, in contrast with **C**^{1}(LiOTf), the ^{13}C NMR chemical shift of the lithium adducts, in the latter cases, were high field shifted by only a few ppm. This clearly indicates that the coordination of lithium to **C**^{1} more strongly perturbs the electronic structure. Attempts to remove the lithium triflate by extraction into less polar solvents were unsuccessful, sequestration by [12]crown-4 had no effect, and all attempts to obtain single crystals of **C**^{1}(LiOTf) failed. However, addition of triphenyl borane at −78 °C led to the corresponding borane adduct **C**^{1}(BPh$_3$), which was isolated as red single crystals in 53% yield (Figure 2). Note that the carbon signal of Cα ($\delta = 75$ ppm) is high field shifted by 115 ppm relative to that observed for **C**^{1}(LiOTf), indicating a considerable structural change.

Allenylidene adduct **C**^{1}(LiOTf) did not appear to be an efficient precursor for transmetalation reactions. However, there have been many reports in which imidazolium and triazolium salts were deprotonated with silver bases, to form directly the corresponding NHC silver complexes, which readily undergo transmetalation reactions with a large variety of metals.[26] Therefore, salt **2** (X = I$^-$) was treated with silver oxide and complex [(**C**^{1})$_2$Ag^I]$^+$·I$^-$ was obtained as red-brown needles in 72% yield (Figure 3). The ^{109}Ag NMR signal appeared at $\delta = 856.2$ ppm, in the range reported for NHC silver complexes,[27] but the carbon–silver bond is shorter (2.026(10) Å versus 2.05-2.18 Å).[26] This effect is most likely caused by the increased s character of the lone pair donating to the metal (sp as opposed to sp^2 hybridized). Additionally, the terminal carbon–carbon bond is only slightly shorter (1.235(15) Å) than that calculated for the free species **C**^{1} (1.26 Å). As expected, the CCC skeleton remains nearly linear (178.8 (10)° at Cα and 176.8(10)° at Cβ), and the two allenylidenes are ligated essentially linearly around the metal center (179.0(4)°).

With silver complexes [(**C**^{1})$_2$Ag^I]$^+$ in hand, we first tested a transmetalation reaction with palladium, which is ubiquitous in late-transition-metal chemistry. Tetrakis(triphenylphosphine)palladium(0) was added to one equivalent of [(**C**^{1})$_2$Ag^I]BF$_4$, and the palladium complex [(**C**^{1})$_2$Pd^{II}]$^{2+}$ was isolated in 51% yield (Figure 4, left). The results of the X-ray diffraction study show that two phosphine groups have been substituted by two allenylidenes **C**^{1}. Interestingly, the palladium center has been formally oxidized from 0 to +2, probably by silver(tetrafluoroborate) generated during the transmetalation reaction, to form this square-planar complex. The palladium–carbon bond length (1.986(2) Å) lies at the shorter end of the range of Pd−C bond lengths found in

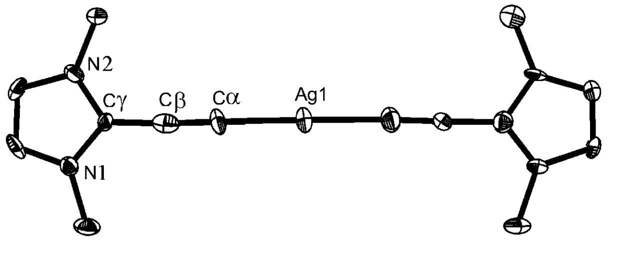

Figure 3. X-ray crystal structures of [(**C**^{1})$_2$Ag^I]I. Hydrogen atoms, I$^-$ anion, and the solvent molecules of crystallization are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag1–Cα 2.026(10), Cα–Cβ 1.235(15), Cβ–Cγ 1.408(15), Cγ–N1 1.343(12), Cγ–N2 1.351(13); N1-Cγ-N2 107.0(8), Ag1-Cα-Cβ 178.8(10), Cα-Cβ-Cγ 176.8(10), Cα-Ag1-Cαa 179.0(4).

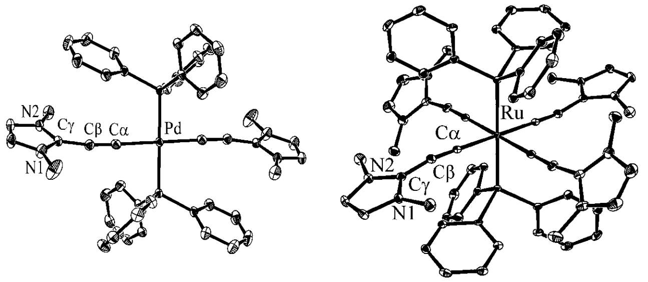

Figure 4. X-ray crystal structures of $[(\mathbf{C}^1)_2\mathrm{Pd}^{II}]^{2+}$ (left) and $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$ (right). Hydrogen atoms, counterions (BF_4^- and $\mathrm{Ag}_2\mathrm{I}_4^{2-}$, respectively), and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]. $[(\mathbf{C}^1)_2\mathrm{Pd}^{II}]^{2+}$: Pd–Cα 1.986(2), Cα–Cβ 1.199(3), Cβ–Cγ 1.408(3), Cγ–N1 1.338(2), Cγ–N2 1.344(2); N1-Cγ-N2 107.33(16); Pd-Cα-Cβ 178.39(19), Cα-Cβ-Cγ 171.6(2), Cα-Pd1-Cαa 180.00(12). $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$: Ru–Cα 2.027(4), Cα–Cβ 1.226(7), Cβ–Cγ 1.395(6), Cγ–N1 1.355(6), Cγ–N2 1.355(6); N1-Cγ-N2 106.2(4); Ru-Cα-Cβ 177.1(4), Cα-Cβ-Cγ 172.0(5), Cα-Ru1-Cαa 180.00(12).

NHC–palladium complexes[28] and is similar to that reported for the only known allenylidene Pd complex (1.925 Å).[17]

Next, we selected ruthenium as a metal center because of the considerable interest of allenylidene ruthenium complexes in homogeneous catalysis.[13] In this case, tris(triphenylphosphine)ruthenium dichloride was mixed with $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]\mathrm{OTf}$ in dichloromethane in the presence of sodium iodide (in an effort to sequester the silver and prevent possible reduction of the metal). An X-ray diffraction study shows that the tetrakis(allenylidene)bis(triphenylphosphine)ruthenium(II) complex $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$ was formed (Figure 4, right).[29] The metal center was not reduced, but silver did act as a halogen scavenger to give the octahedral structure with two axial phosphines and four of the small allenylidenes $\mathbf{C}^1$ symmetrically placed equatorially. Once again nearly linear allenylidene ligands, with terminal and internal angles of 177.1(4)° and 172.0(5)°, respectively, were observed. The insolubility of $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$ made typical solution-state NMR spectroscopy extremely difficult. Therefore, to further characterize compound $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$, MAS NMR spectroscopy was used, and thanks to the cross polarization the quaternary carbon atom bonded to the ruthenium center is visible at $\delta = 189.2$ ppm, which is near the chemical shift of the lithium complex $\mathbf{C}^1(\mathrm{LiX})$.

Although a free allenylidene of type **C** seems difficult to isolate, the synthesis of the first silver allenylidene complex $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]^+$ opens very interesting perspectives for the synthesis of a variety of synthetically and catalytically useful allenylidene transition-metal complexes, as demonstrated by the preparation of the palladium and ruthenium complexes $[(\mathbf{C}^1)_2\mathrm{Pd}^{II}]^{2+}$ and $[(\mathbf{C}_1)_4\mathrm{Ru}^{II}]^{2+}$.

Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques.

Synthesis of imidazolium triflate **2** ($\mathrm{X} = \mathrm{TfO}^-$): To a solution (15 mL) of 2-ethynyl-1-methyl imidazole **1** (2.7 g, 25.4 mmol) in $\mathrm{CH_2Cl_2}$ was added methyl trifluoromethanesulfonate (2.9 mL, 25.4 mmol). The mixture was stirred at room temperature for 12 h. All volatile compounds were removed under vacuum, and the resulting solid washed with diethyl ether and dichloromethane to give imidazolium salt **2** ($\mathrm{X} = \mathrm{TfO}^-$) as a dark brown solid (442 mg, 6 %) (a similar procedure was used with methyl iodide or trimethyloxonium tetrafluoroborate); m.p.: 168–171 °C; ^{1}H NMR ($\mathrm{CD_3CN}$, 25 °C, 600 MHz): $\delta = 3.87$ (s, 6 H, $\mathrm{CH_3}$), 4.74 (s, 1 H, $\mathrm{C{\equiv}CH}$), 7.42 ppm (s, 2 H, $=$CH); ^{13}C NMR ($\mathrm{CD_3CN}$, 25 °C, 151 MHz): $\delta = 36.2$ ($\mathrm{CH_3}$), 63.9 ($C{\equiv}$CH), 96.8 ($\mathrm{C{\equiv}}C$H), 121.1 (q, $J_{\mathrm{CF}} = 320.7$ Hz, $\mathrm{CF_3}$), 124.2 ($=$CH), 129.2 ppm (C-$\mathrm{C{\equiv}CH}$).

Synthesis of allenylidene lithium adduct $\mathbf{C}^1(\mathrm{LiOTf})$: A 1.6 M solution of nBuLi (380 mL, 0.61 mmol) in pentane was added to imidazolium salt **2** ($\mathrm{X} = \mathrm{TfO}^-$) (150 mg, 0.55 mmol) in THF (5 mL) at −78 °C. The mixture was stirred for 30 min and then allowed to warm to room temperature; ^{1}H NMR ([D$_8$]THF, 25 °C, 600 MHz): $\delta = 3.71$ (s, 6 H, $\mathrm{CH_3}$), 7.22 ppm (s, 2 H, CH); ^{7}Li ([D$_8$]THF, 25 °C, 233 MHz): $\delta = 0.66$ ppm; ^{13}C NMR ([D$_8$]THF, 25 °C, 151 MHz): $\delta = 35.6$ ($\mathrm{CH_3}$), 90.6 ($C{\equiv}$C-Li), 120.7 ($=$CH), 121.8 (q, $J_{\mathrm{CF}} = 320.0$ Hz, $\mathrm{CF_3}$), 133.6 (C-$\mathrm{C{\equiv}CH}$), 190.2 ppm ($\mathrm{C{\equiv}}C$-Li).

Synthesis of allenylidene borane adduct $\mathbf{C}^1(\mathrm{BPh_3})$: To a freshly prepared solution (3 mL) of lithium salt $\mathbf{C}^1(\mathrm{LiOTf})$ in THF [prepared from triflate salt **2** (118 mg, 0.436 mmol) and nBuLi (1.6 M, 0.273 mL)] at −78 °C was added triphenyl borane (106 mg, 0.436 mmol) in THF (3 mL). The solution was stirred for 4 h and allowed to warm to room temperature. All volatile compounds were removed under vacuum, and the resultant solid was washed with diethyl ether (2 × 10 mL). The product was extracted in dichloromethane. A concentrated dichloromethane solution was layered with diethyl ether to give red single crystals of $\mathbf{C}^1(\mathrm{BPh_3})$ (84 mg, 53 %); m.p.: 113–115 °C; ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C, 600 MHz): $\delta = 3.66$ (s, 6 H, $\mathrm{CH_3}$), 6.63 (s, 2 H, CH), 6.90–7.81 ppm (m, 15 H, Ph); ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 25 °C, 151 MHz): $\delta =$ 35.8 ($\mathrm{CH_3}$), 75.5 (broad, $\mathrm{C{\equiv}}C$-B), 96.7 ($C{\equiv}$C-B), 120.6 ($=$CH), 123.5, 126.6, 134.3, and 158.4 (broad) (PhB), 161.7 ppm (C-$\mathrm{C{\equiv}CB}$); ^{11}B ($\mathrm{CD_2Cl_2}$, 25 °C, 233 MHz): $\delta = -11.7$ ppm.

Synthesis of allenylidene silver complex $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]^+$: Imidazolium iodide salt **2** (296 mg, 1.19 mmol) and $\mathrm{Ag_2O}$ (500 mg, 2.16 mmol) were stirred together in acetonitrile (7 mL) for 12 h. The resulting solution was filtered through celite, then all volatile compounds were removed under vacuum, and the dark solid washed with diethyl ether. Crystallization from dichloromethane at −30 °C gave $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]\mathrm{I}$ as red-brown needles (408 mg, 72 %); m.p.: 139–140 °C; ^{1}H NMR ($\mathrm{CD_3CN}$, 25 °C, 600 MHz): $\delta = 3.83$ (s, 6 H, $\mathrm{CH_3}$), 7.32 ppm (s, 2 H, CH); ^{13}C NMR ($\mathrm{CD_3CN}$, 25 °C, 151 MHz): $\delta = 37.0$ ($\mathrm{CH_3}$), 96.7 ($C{=}\mathrm{C{=}Ag}$), 123.8 ($=$CH), 130.8 ppm (CCCAg), (CAg not observed); ^{109}Ag NMR ($\mathrm{CD_3CN}$, 25 °C, 27.9 MHz): $\delta = 856.2$ ppm; high-resolution mass spectrometry: FAB m/z 347.0411 (expected: 347.0420).

Synthesis of allenylidene palladium complex $[(\mathbf{C}^1)_2\mathrm{Pd}^{II}]^{2+}$: To a mixture of $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]\mathrm{BF_4}$ (159 mg, 0.37 mmol) and tetrakis(triphenylphosphine)palladium (0.422 g, 0.37 mmol) was added acetonitrile (3 mL). The solution was allowed to react for 12 h and then evaporated to dryness. The residue was then extracted in dichloromethane and concentrated. Yellow crystals of $[(\mathbf{C}^1)_2\mathrm{Pd}^{II}]^{2+}$ formed at −30 °C (194 mg, 51 %); m.p.: 208–210 °C; ^{31}P NMR ($\mathrm{CDCl_3}$, 25 °C, 242 MHz): $\delta = 26.2$ ppm; ^{1}H NMR ($\mathrm{CD_3CN}$, 25 °C, 600 MHz): $\delta =$ 2.96 (s, 12 H, $\mathrm{CH_3}$), 6.90 (s, 4 H, CH), 7.1–7.8 ppm (m, 30 H, $\mathrm{PPh_3}$); ^{13}C NMR ($\mathrm{CD_3CN}$, 25 °C, 151 MHz): $\delta = 34.5$ ($C\mathrm{H_3}$), 93.1 ($C{=}\mathrm{C{=}Pd}$), 122.3 (s, $=$CH), 128.7, 131.2, 134.4 [s (broad), PPh], 140.1 ppm (s, CCCPd), $C{=}$Pd not observed; high-resolution mass spectrometry: FAB [M+$\mathrm{BF_4}$] m/z 957.2252 (expected 957.2256).

Synthesis of allenylidene ruthenium complex $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$: $[(\mathbf{C}^1)_2\mathrm{Ag}^{I}]\mathrm{OTf}$ (0.140 g, 0.28 mmol), dichlororuthenium tris(triphenylphosphine) (0.135 g, 0.14 mmol), and sodium iodide (0.084 g, 0.56 mmol) were mixed in dichloromethane (5 mL) and stirred for 12 h at room temperature. The solution was filtered through celite, and the solvent was removed under vacuum. Pale yellow crystals of $[(\mathbf{C}^1)_4\mathrm{Ru}^{II}]^{2+}$ were grown in acetonitrile at room temperature (82 mg, 32 %); m.p.: 158–160 °C; ^{31}P MAS NMR (25 °C, 162 MHz): $\delta = 42.0$; ^{13}C MAS NMR (25 °C, 101 MHz): $\delta = 37.9$ ($\mathrm{CH_3}$), 96.7 ($C{=}\mathrm{C{=}Ru}$), 121.9 (=CH), 129.7–140.6 (m, PPh_3), 144.1 (*C*CCRu), 189.2 ppm (*C*=Ru).

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