except that the rates to and from CIP **7** are slow enough that dissociation of **7** to **8** is faster than the exchange process (**5a**/**5b** exchange is faster than the dissociation of **3** by about a factor of 10^3).

In summary, DNMR studies have shown that the Li/Te exchange of the lithiothiophene **1** with the telluride **2** proceeds exclusively through the ate complex **3**. The very fast intramolecular Li/Se exchange of **5a** and **5b**, on the other hand, does not proceed appreciably through the observable SIP ate complex **6**. We propose that here the SIP/CIP interconversion is slower than the Li/Se exchange rate, and this allows the intramolecular substitution to bypass the SIP of **6**.

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[13] The exchange of Ar_2Te with Ar_3TeLi in 1,3-dioxolane/2-methyltetrahydrofuran/HMPA solution was shown to be first order in $[Ar_2Te]$ by DNMR experiments with variable telluride concentrations, as expected for process 2. Under conditions for which the formation constant of the ate complex is large, such as in the presence of several equivalents of HMPA,[1g] the exchange between Ar_2Te and the ate complex by process 1 would be zero order in $[Ar_2Te]$.

[14] The exchange matrix for the simulations in Figure 1 and Figure 3 and the relationship between the NMR rate constants (k_{AB}, k_{AC}, etc.) and the physical rate constants of Equations (1)–(4) (k_{ate} is first order; k_{pseudo}, k_{dian}, k_M, and k_d are second order) are given below (in the simulations of Figure 1, k_{pseudo}, k_{dian}, and k_d were set to zero).

[15] The appearance of the signal assigned to **6** was fully reversible and strongly temperature dependent (in 1/1/1 ether/dimethyl ether/THF at −60°C: >80% **5**; at −143°C: ca. 60% **6**). Conversion to **6** (δ_{Se} = 403 ppm) was quantitative if excess HMPA was added (δ_{Se} = 409 ppm), an effect also seen for the parent system (without the isopropyl substituent)[1c] and for other Te, I, and Sn ate complexes.[1a,d,g] The signals of the two apical C atoms of **6** were characteristically shifted downfield (δ = 181.9, 187.2 ppm), as was also seen for numerous other ate complexes.[1b] Quenching of the HMPA solution of **6** with bromotrimethylstannane cleanly gave the stannylated precursors (2:1 mixture), that is, no structural changes had occurred.

Generation of Polyunsaturated Cumulene Chains by Unprecedented Insertions of the Ynamine $MeC\equiv CNEt_2$ in Ruthenium(II) Allenylidene Complexes[**]

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Maria Pilar Gamasa, Jose Gimeno,* and
Santiago García-Granda

Allenylidene (propadienylidene) complexes $[ML_n]{=}C{=}C{=}CR^1R^2$, which belong to the series of unsaturated carbenes $[ML_n]{=}C({=}C)_i{=}CR^1R^2$ ($i > 0$) have received increasing interest during the last few years.[1] These derivatives have a great potential to promote novel carbon–carbon and carbon–heteroatom coupling reactions, because of the electrophilic (C_α and C_γ) and nucleophilic (C_β) character of the carbon nuclei of the allenylidene chain. While simple nucleophilic and electrophilic additions are well-studied, cycloaddition processes are scarce, in particular those involving $C\equiv C$ dipolar substrates.[2] In 1998 Fischer and co-workers reported the synthesis of cyclobutenylidene and alkenylallenylidene Group 6 metal complexes which are formed as a mixture by the cycloaddition of ynamines to both the $C_\alpha{=}C_\beta$ and $C_\beta{=}C_\gamma$ bonds of an

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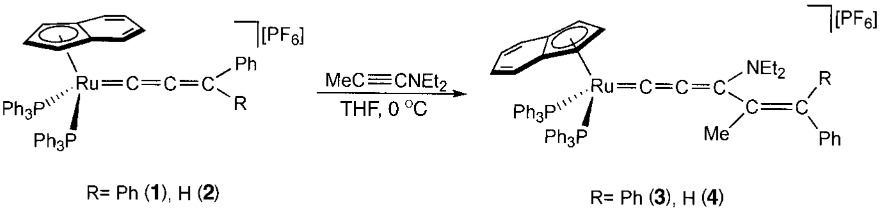
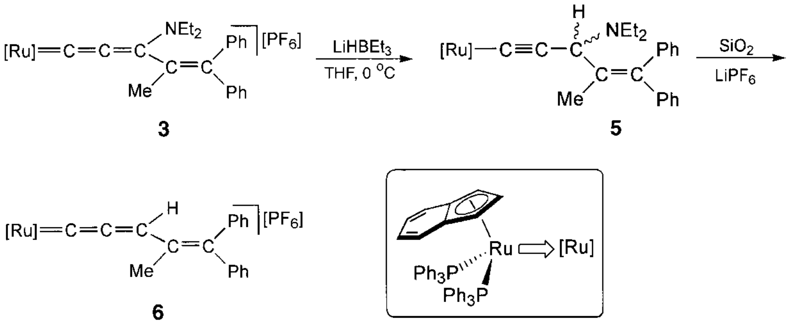
allenylidene chain, respectively.[2a] During our investigations into the reactivity of indenyl–allenylidene complexes [Ru(=C=C=CR^{1}R^2)(η^5-C_9H_7)(PPh_3)$_2$][PF_6] we have shown that the addition of nucleophiles to the unsaturated chain takes place regioselectively at the C_γ. C_α atom of the cumulene moiety is sterically protected by the bulky phosphane and the indenyl group.[3] This regioselectivity prompted us to study cycloaddition reactions as a synthetic approach to highly unsaturated alkenylallenylidene derivatives. Herein we report that not only does this process occur selectively, but it is also a synthetic methodology of unprecedented polyalkenyl allenylidene chains =C=C=C(R)–(CH=CMe)$_n$–C(Me)=CPh$_2$ (n = 1,2; R = H, NEt$_2$) which notably, is high yielding, sequential, and stereoselective.

Allenylidene indenylruthenium(II) complexes **1** or **2**[4] react immediately with an excess of the ynamine MeC≡CNEt$_2$[5] in THF at 0 °C, yielding the alkenyl(amino)allenylidene complexes **3** and **4** regio- and stereoselectively [6] as orange crystalline air-stable solids in nearly quantitative yield (Scheme 1).[7] The most distinctive features of the spectroscopic data are the characteristic ν(C=C=C) absorption band at 1989 cm^{-1} and the three downfield signals for the allenylidene carbon nuclei in the ^{13}C{^{1}H} NMR spectra which appear in the range δ = 199.39–206.68 (C_α), 155.26–156.79 (C_β), and 121.72–122.76 ppm (C_γ). Conclusive 2D NMR (NOESY) experiments for complex **4** showed that the hydrogen and methyl substituents are in a *trans* arrangement. The formation of **3** and **4** probably proceeds through an initial addition of the ynamine at the C_γ atom of the cumulene moiety, which leads to the formation of a cationic alkynyl intermediate complex. Further ring closure, which involves the C_β atom, gives the [2+2] vinylidene cycloadduct. A subsequent cycloreversion reaction yields the alkenyl(amino)allenylidenes **3** and **4**. An analogous mechanism was also proposed in the cycloaddition of ynamines with Group 6 allenylidene complexes.[2a]



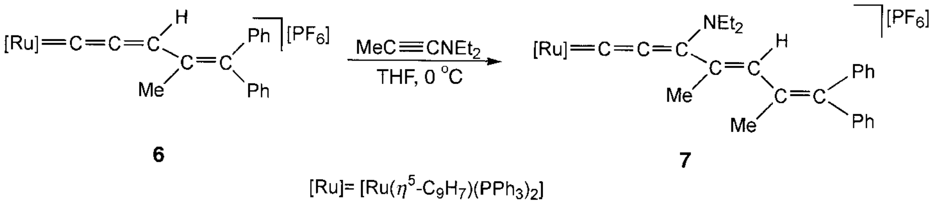
Scheme 1.

It is interesting that alkenyl(amino)allenylidenes, in contrast to the allenylidene precursors **1** and **2**, are not prone to further insertions despite the presence of an excess of the ynamine. This is probably because of the alkynyl character of the organic chain in **3**.[8] To facilitate further insertion reactions, we set up the transformation of the amino allenylidene **3** into the corresponding secondary derivative **6**, which was obtained in two steps via the unstable alkynyl derivative **5**,[6] from the treatment of **3** with a slight excess of LiBHEt$_3$ in THF, followed by purification on a short silica column (Scheme 2). Complex **6**[6] is isolated as a violet microcrystalline powder (86 %). Characterization of **6** is supported by the spectroscopic data which can be compared to those of the parent allenylidene complex **2** (ν(C=C=C) = 1932 cm^{-1}; Ru=C=C=C carbon resonances at δ = 295.05 (C_α), 208.84 (C_β), and 150.61 ppm(C_γ)).



Scheme 2.

Complex **6** reacts with 2 equivalents of ynamine MeC≡CNEt$_2$, in a way analogous to the above-described allenylidene complex **2**, affording the butadienyl(amino)allenylidene complex **7**,[6] isolated (80 %) as an air-stable orange solid (Scheme 3). IR and NMR spectroscopic data for **7** indicate the presence of the cumulene moiety and the insertion of the ynamine. It is remarkable that the insertion proceeds in a regio- and stereoselective manner, because only one isomer is obtained. The structure of **7** has been unambiguously confirmed by X-ray diffraction (Figure 1).[9] The main feature of the molecular structure is the *s-trans*, *s-trans* stereochemistry of the butadienyl-allenylidene chain arrangement in which the metal–cumulene moiety is *trans* to the terminal diphenyl–alkenyl group fragment. The plane including the butadienyl fragment C4-C5-C6-C7 is almost perpendicular (99.2(3)°) to that defined by C2-C3-N1, which is probably the appropriate orientation to minimize the repulsive interactions between the diethylamino group and the substituents at the C–C double bonds.[10]



Scheme 3.

These sequential processes constitute an efficient synthetic methodology for building up a butadienyl–allenylidene chain. We have succeeded in preparing a higher unsaturated chain by following an identical synthetic procedure. Thus, the

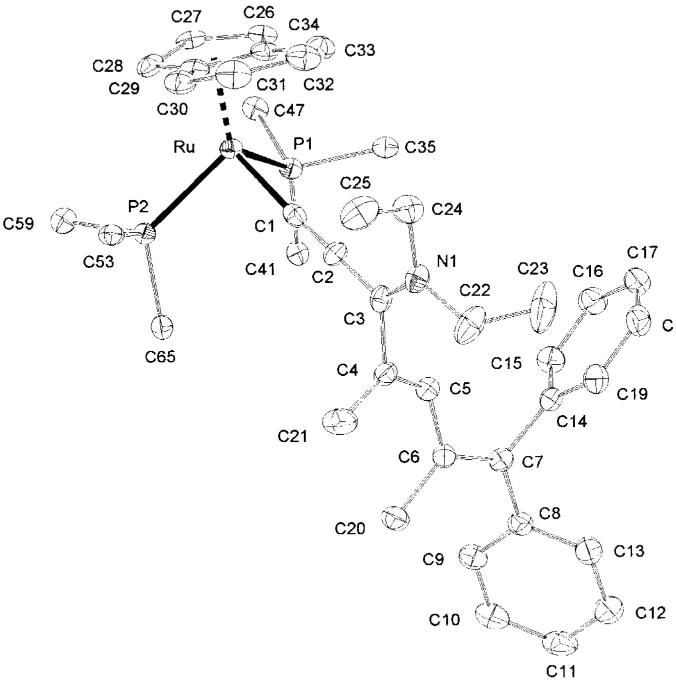
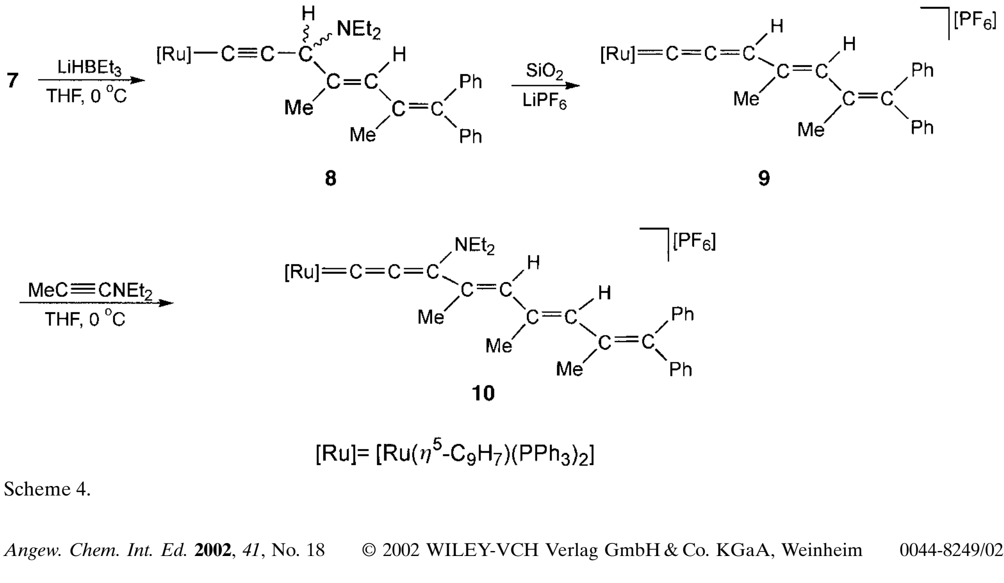


Figure 1. Molecular structure for the cation of complex **7** (ORTEP plot). Selected bond lengths [Å] and angles [°]: Ru-P1 2.299(9), Ru-P2 2.305(9), Ru-C1 1.946(4), C1-C2 1.229(5), C2-C3 1.390(5), C3-C4 1.500(5), C4-C5 1.340(6), C5-C6 1.510(5), C6-C7 1.355(5), C3-N1 1.319(5); Ru-C1-C2 174.6(3), C1-C2-C3 177.8(4), C2-C3-N1 122.1(3), C4-C3-N1 119.0(3), C2-C3-C4 118.4(2).

reaction of **7** with one equivalent of $\mathrm{LiHBEt_3}$ in THF, followed by treatment of the resulting alkynyl complex **8** solution (characterized by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$, $^{1}\mathrm{H}$, and $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectroscopy) with silica, yields the desired secondary butadienyl–allenylidene complex **9**, which is isolated as a violet solid in 83 % yield after workup (see Scheme 4). Complex **9** also reacts with $\mathrm{MeC{\equiv}CNEt_2}$ in THF at 0 °C yielding the hexatrienyl(amino)allenylidene complex **10** regio- and stereoselectively[6] as an orange solid (45 %; Scheme 4). Complexes **9** and **10** have been fully characterized by elemental analysis, and IR and NMR spectroscopy. In particular, the $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum and NOESY experiments for **10** are comparable to those of **7**, and support the *all-trans* stereochemistry of the substituents in the conjugated C=C chain.

These stereoselective sequential insertions of ynamines into allenylidene moieties have disclosed an unprecedented synthetic approach of polyunsaturated cumulene chains.



Scheme 4.

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[6] Selected spectroscopic data: **3**: Yield: 1.03 g, 87 %; IR (KBr): $\tilde{\nu} = 1989$ (C=C=C) $\mathrm{cm^{-1}}$; $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.44 MHz, $\mathrm{CDCl_3}$, 18 °C): 49.50 (d, $^{2}J(\mathrm{P,P}) = 27.5$ Hz), 49.35 ppm (d, $^{2}J(\mathrm{P,P}) = 27.5$ Hz); $^{1}\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 0.94$ (virtual t, $^{3}J(\mathrm{H,H}) = 7.1$ Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.06 (virtual t, $^{3}J(\mathrm{H,H}) = 7.1$ Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.79 (s, 3 H; $=\mathrm{CCH_3}$), 3.17 (m, 1 H; $\mathrm{C}H_2\mathrm{CH_3}$), 3.45 (m, 1 H; $\mathrm{C}H_2\mathrm{CH_3}$), 3.73 (m, 1 H; $\mathrm{C}H_2\mathrm{CH_3}$), 4.12 ppm (m, 1 H; $\mathrm{C}H_2\mathrm{CH_3}$); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.47 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 11.74$ (s; $\mathrm{CH_2}C\mathrm{H_3}$), 12.94 (s; $\mathrm{CH_2}C\mathrm{H_3}$), 20.22 (s; $=\mathrm{C}C\mathrm{H_3}$), 45.75 (s; $C\mathrm{H_2CH_3}$), 47.11 (s; $C\mathrm{H_2CH_3}$), 121.72 (s; C_β), 126.05–142.20 (m, $\mathrm{C_{arom}}$; $=C\mathrm{CH_3}$, $=C\mathrm{Ph_2}$,), 155.26 (s; $\mathrm{C}_\gamma\mathrm{N}$), 199.39 ppm (virtual t, $^{2}J(\mathrm{C,P}) = 20.7$ Hz; $\mathrm{Ru{=}C}_\alpha$). **5:** $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($[\mathrm{D_8}]$THF): $\delta = 52.43$ (d, $^{2}J(\mathrm{P,P}) = 34.0$ Hz), 52.73 ppm (d, $^{2}J(\mathrm{P,P}) = 34.0$ Hz); $^{1}\mathrm{H}$ NMR ($[\mathrm{D_8}]$THF): $\delta = 0.80$ (m, 6 H; $\mathrm{CH_2C}H_3$), 1.99 (s, 3 H; $\mathrm{CH_3}$), 2.65 (q, $^{3}J(\mathrm{H,H}) = 6.8$ Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 2.72 (q, $^{3}J(\mathrm{H,H}) = 6.8$ Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 4.42 ppm (s, 1 H; CH); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($[\mathrm{D_8}]$THF): $\delta = 10.82$ (s; $\mathrm{CH_2}C\mathrm{H_3}$), 16.82 (s; $=\mathrm{C}C\mathrm{H_3}$), 42.09 (s; $C\mathrm{H_2CH_3}$), 58.79 (s; $\mathrm{C}_\gamma\mathrm{H}$), 93.60 (virtual t, $^{2}J(\mathrm{C,P}) = 22.7$ Hz; Ru-C_α), 142.89 (s; $=C\mathrm{CH_3}$ and $=C\mathrm{Ph_2}$), 143.94 ppm (s; $=C\mathrm{CH_3}$ and $=C\mathrm{Ph_2}$). **6**: Yield: 0.53 g, 86 %, IR (KBr): $\tilde{\nu} = 1932$ (C=C=C) $\mathrm{cm^{-1}}$; $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.44 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 46.99$ ppm (s); $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$): $\delta = 2.30$ (s, 3 H; $=\mathrm{CCH_3}$), 8.34 ppm (s, 1 H; =C=C=CH); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.47 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 19.13$ (s; $=\mathrm{C}C\mathrm{H_3}$), 126.47–142.35 (m, $\mathrm{C_{arom}}$; $=C\mathrm{CH_3}$), 150.61 (s; C_γ), 161.70 (s; $=C\mathrm{Ph_2}$), 208.84 (s; C_β), 295.05 ppm (t, $^{2}J(\mathrm{C,P}) = 19.7$ Hz; $\mathrm{Ru{=}C}_\alpha$). **7**: Yield: 0.49 g, 80 %; IR (KBr): $\tilde{\nu} = 1992$ $\mathrm{cm^{-1}}$ (C=C=C); $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): $\delta = 49.40$ ppm (s); $^{1}\mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 1.08$ (t, $^{3}J(\mathrm{H,H}) = 6.8$ Hz,

3 H; $\mathrm{CH_2C}H_3$), 1.21 (t, ^3J(H,H) = 6.8 Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.51 (s, 3 H; $=\mathrm{CCH_3}$), 1.86 (s, 3 H; $=\mathrm{CCH_3}$), 3.08 (q, ^3J(H,H) = 6.8 Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 3.76 (q, ^3J(H,H) = 6.8 Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 5.88 ppm (s, 1 H; =CH); ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 12.90$ (s; $\mathrm{CH_2}C\mathrm{H_3}$), 13.78 (s; $\mathrm{CH_2}C\mathrm{H_3}$), 17.33 (s; $=\mathrm{C}C\mathrm{H_3}$), 20.60 (s; $=\mathrm{C}C\mathrm{H_3}$), 45.91 (s; $C\mathrm{H_2CH_3}$), 47.02 (s; $C\mathrm{H_2CH_3}$), 121.07 (s; C_β), 126.98–143.33 (m; $\mathrm{C_{arom}}$, $=C\mathrm{CH_3}$, $=C\mathrm{Ph_2}$), 132.41 (s; =CH), 156.21 (s; C_γN), 202.21 ppm (t, ^2J(C,P) = 21.2 Hz; Ru = C_α). **10:** Yield: 0.14 g, 45 %, IR (KBr): $\tilde{\nu} =$ 1990 (C=C=C) cm^{-1}; ^{31}P{^{1}H} NMR (121.44 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta =$ 49.59 ppm (s); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 1.26$ (t, ^3J(H,H) = 7.4 Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.31 (t, ^3J(H,H) = 7.4 Hz, 3 H; $\mathrm{CH_2C}H_3$), 1.49, 1.65 (s, 3 H; $=\mathrm{CCH_3}$), 1.88 (s, 3 H; $=\mathrm{CCH_3}$), 3.54 (q, ^3J(H,H) = 7.4 Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 3.88 (q, ^3J(H,H) = 7.4 Hz, 2 H; $\mathrm{C}H_2\mathrm{CH_3}$), 5.50 (s, 1 H; =CH), 5.97 ppm (s, 1 H; =CH); ^{13}C{^{1}H} NMR (75.47 MHz, $\mathrm{CDCl_3}$, 18 °C): $\delta = 13.02$ and 13.76 (s; $\mathrm{CH_2}C\mathrm{H_3}$), 16.78 (s; $=\mathrm{C}C\mathrm{H_3}$), 18.22 (s; $=\mathrm{C}C\mathrm{H_3}$), 21.09 (s; $=\mathrm{C}C\mathrm{H_3}$), 46.40 (s; $C\mathrm{H_2CH_3}$), 47.55 (s; $C\mathrm{H_2CH_3}$), 121.14 (s; C_β), 126.60–143.18 (m; Ph, $=C\mathrm{CH_3}$, $=C\mathrm{Ph_2}$, =CH), 157.11 (s; C_γN), 202.61 ppm (t, ^2J(C,P) = 21.5 Hz; Ru=C_α).

[7] Other vinyl allenylidene complexes are known: D. Péron, A. Romero, P. H. Dixneuf, *Organometallics* **1995**, *14*, 3319; D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab, P. H. Dixneuf, *Organometallics* **1995**, *14*, 5263.

[8] ^{13}C{^{1}H} NMR (RuC_α) $\delta = 199.39$ (**3**) versus 295.05 ppm (**6**) and $\tilde{\nu}$(C=C=C) 1989 (**3**) versus 1932 cm^{-1} (**6**).

[9] Data for the X-ray structure analysis for **7:** Crystal from MeOH/$\mathrm{CH_2Cl_2}$/pentane, $\mathrm{C_{70}H_{64}F_6NP_3Ru}$ ($M_\mathrm{r} = 1227.20$); crystal size $0.37 \times 0.27 \times 0.20$ mm^3; orthorhombic, space group $P2_12_12_1$ $a =$ 14.41810(10), $b = 14.57510(10)$, $c = 28.23070(10)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 4$, $V = 5932.55(6)$ Å^3, $\rho = 1.374$ g cm^{-3}; $T = 200(2)$ K; $2\Theta_\mathrm{max.} = 68.2°$; 95 891 reflections measured, 10 850 unique ($R_\mathrm{int.} =$ 0.000), and 9859 observed ($I > 2\sigma(I)$); Nonius KAPPA-CCD diffractometer, $\mathrm{Cu_{K\alpha}}$ radiation ($\lambda = 1.54184$ Å), graphite monochromator; multiscan absorption corrections (Ψ scan, min. transmission 79.67 %). The structure was solved by DIRDIF and refined with the full-matrix, least-squares method; $R_1 = 0.00397$, $wR_2 = 0.0999$ (for 9859 reflections with $I > 2\sigma(I)$), $R_1 = 0.0437$, $wR_2 = 0.1035$ (for all data); residual electron density $+0.678/-0.759$ e Å^{-3}. CCDC-179713 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[10] Interatomic distances and angles of the cumulene moiety, as well as those of the rest of the unsaturated chain, are usual for this type of carbon–carbon connectivity (see ref. [1]).

C_8K-Promoted Self-Condensation and Self-Condensation-Cycloisomerization Reactions of α,β-Unsaturated Fischer Carbene Complexes[**]

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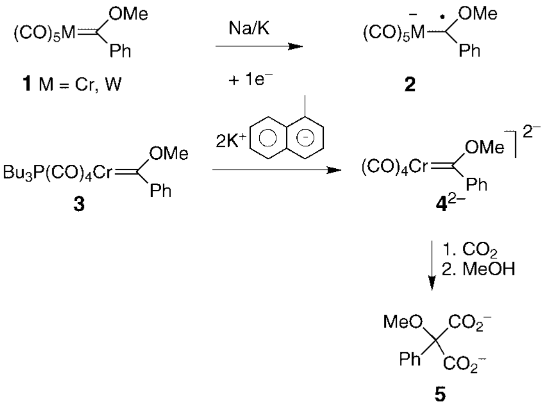
Dedicated to Professor William M. Horspool

The chemistry of stabilized Group 6 metal carbene complexes (Fischer carbenes) has reached a high level of maturity and carbenes have become very valuable building blocks in organic synthesis.[1] In spite of this, the reactivity of highly reduced Fischer carbene complexes has been somewhat neglected. The one-electron reduction of the Group 6 alkoxyaryl carbene complexes **1** by Na/K alloy was originally reported by Casey.[2] In this case, radical anion species **2** stable in diluted THF/hexamethyl phosphoramide (HMPA) solutions were detected by ESR spectroscopy. Further, Cooper and Lee[3] reported the reaction of [$\mathrm{Bu_3P(CO)_4CrC(OMe)Ph}$] (**3**), with potassium 1-methylnaphthalenide to yield the highly reduced carbene complex **4**$^{2-}$ (Scheme 1). This species **4**$^{2-}$ shows the expected umpolung at the carbene carbon atom (which becomes a nucleophile as a result of the increased



Scheme 1.

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