Novel Allenylidene Alkynyl and Ammonia Alkynyl Metal Complexes *via* Selective Synthesis of Mono and Bis Alkynyl Ruthenium(II) Complexes; Crystal Structure of *trans*-[Ru(NH$_3$)(C≡CPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]PF$_6$

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The activation of terminal alkynes with *cis*-[RuCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] leads either to mono alkynyl, *via* vinylidene complex, or to bis alkynyl ruthenium complexes that are the key precursors of *trans*-[Ru(NH$_3$)(C≡CR)-(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]PF$_6$ and [(Ph$_2$C=C=C=RuC≡CPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]PF$_6$ derivatives.

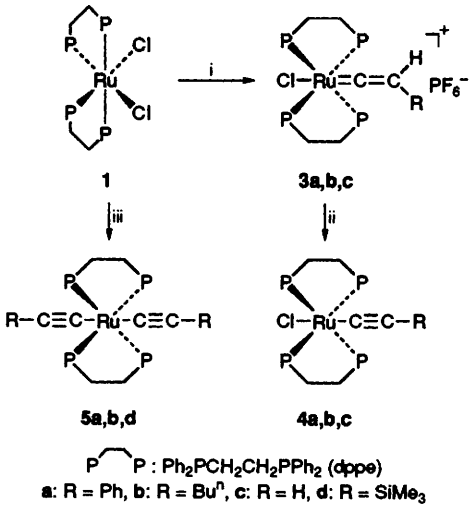
Vinylidene and allenylidene metal intermediates attract interest as the initial species of the activation of terminal alkynes[1] and propynylic alcohol derivatives,[2] or for their potential to give access to unsaturated carbene complexes,[3] or to selective carbon–carbon bond formation with alkynyl intermediates.[4] Vinylidene and allenylidene ruthenium moieties are now recognized as active species in new catalytic transformations of terminal alkynes into vinylcarbamates,[5] enynes[6] or butatrienes[7] *via* dimerization, or unsaturated ketones.[8] These high potential catalytic processes motivate the search for the selective production of bis alkynyl, mixed vinylidene alkynyl or allenylidene alkynyl metal transient intermediates or complexes. We now report the selective access either to mono alkynyl, *via* vinylidene complex, or to bis alkynyl derivatives of [RuCl$_2$(dppe)$_2$] (dppe = Ph$_2$-PCH$_2$CH$_2$PPh$_2$), their transformation into the first examples of mixed *trans*-ammonia alkynyl and *trans*-allenylidene alkynyl ruthenium(II) derivatives and the XRD study of *trans*-[Ru(NH$_3$)(C≡CPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]PF$_6$. This study points out the unexpected crucial role of the dppe with respect to the dppm (Ph$_2$PCH$_2$PPh$_2$) ancillary ligands.

The reaction of *cis*-[RuCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] **1** with 2 equiv. of terminal alkynes **2a–c** and of NaPF$_6$ in CH$_2$Cl$_2$ at room temp. afforded orange crystals of the *trans*-vinylidene complexes **3a–c** isolated in 85–90% yield (Scheme 1). The presence of the vinylidene moiety was identified especially on the basis of an IR absorption at 1620 cm^{-1} ($\nu_{C=C}$) and the low field quintuplet resonance in ^{13}C NMR for the (Ru=C=) carbon nucleus [**3a**: δ, 354.5; $^2J_{PC}$, 13 Hz]. The precursor *trans*-[RuCl$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] under analogous conditions also gave the complexes **3a–c** in similar yields. Treatment of **3a–c** with pulverised K$_2$CO$_3$ led to the *trans*-alkynyl derivatives **4a–c** in 70–75% yield. The overall transformation **1** → **3** → **4** can be performed without isolation of **3** and thus appears to be the most straightforward route to monoalkynyl ruthenium complexes **4** that cannot be directly obtained from **1** and classical lithium or Grignard alkynyls.

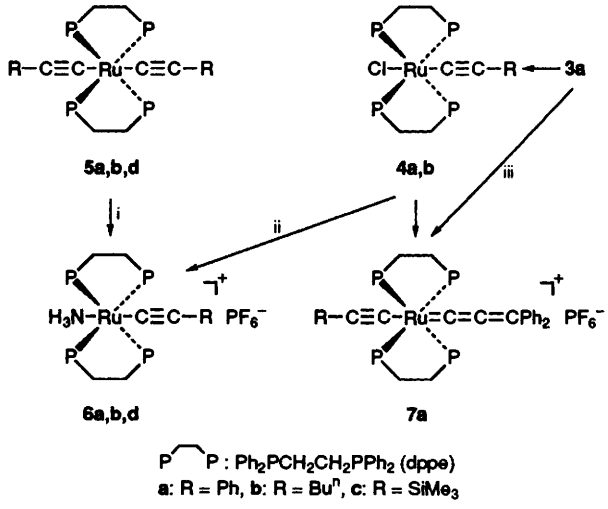
The reaction of precursor **1** with 3 equiv. of **2a** and of NaPF$_6$ and an excess of Et$_3$N in CH$_2$Cl$_2$, by contrast, led to the bis *trans*-alkynyl ruthenium complex **5a** (65%). Analogously the *trans*-bis alkynyl derivatives **5b** (67%) and **5d** (60%) were also prepared. The formation of bis alkynyl **5** probably results from the intermediates **3** and **4** as the presence of NaPF$_6$ is required, but the formation of complexes **5** and **4** with alkynes **2** and NEt$_3$ was obtained only in moderate yield. The convenient route to bis *trans*-alkynyl ruthenium complexes **5**, directly from **1**, contrasts with the inhibition to afford analogous derivatives from the related *cis* to *trans*-[Ru(Cl$_2$(dppm)$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$) precursors.[9] Novel reactivity promoted by the Ru(dppe)$_2$ moiety can be expected as shown by the transformations of **5** into derivatives **6** and **7**.

As vinylidene alkynyl metal complexes are still scarce[4c] we have attempted to produce them simply by protonation of precursors **5** with acids and decomposition takes place. However, when complex **5a** was reacted with NH$_4$PF$_6$ in CH$_2$Cl$_2$, complex **6a**, containing mixed *trans*-ammonia and acetylide ligands, was obtained in 73% yield. Similarly, complexes **6b** and **d** were obtained from **5b** and **d** with NH$_4$PF$_6$ in 70 and 67% yields, respectively (Scheme 2). These amine–ruthenium complexes **6** are relevant to both activation of ammonia and the formation of alkynylamine.

A single crystal X-ray structural analysis was carried out on complex **6a**.† The ORTEP plot (Fig. 1) establishes the *trans*



Scheme 1 *Reagents and conditions*: reactions performed in CH$_2$Cl$_2$ at room temp. i, HC≡CR **2** (2 equiv.), NaPF$_6$ (2 equiv.), 4 h, then crystallization in CH$_2$Cl$_2$–hexane; ii, fourfold excess of K$_2$CO$_3$ and stirring for 4 h; iii, HC≡CR **2** (3 equiv.), NaPF$_6$ (3 equiv.), Et$_3$N (6 equiv.), 4 h



Scheme 2 *Reagents and conditions:* reactions performed in CH$_2$Cl$_2$ at room temp.: i, NH$_4$PF$_6$ (2 equiv.), 24 h; ii, NH$_4$PF$_6$ (2 equiv.) for 72 h; iii, **3a** (0.5 mmol), and HC≡CCPh$_2$OH (0.5 mmol), NaPF$_6$ and Et$_3$N (1 mmol) for 4 h

positions of the NH_3 and acetylide ligands but without colinearity [C(1)–Ru–N 169.1(2)°] and with a normal CC bond distance [1.187(7) Å] but a longer Ru–N bond [2.215(5) Å] than in related complexes [2.159(6) Å] in [Ru–$NH_2CHMe_2(H)(PMe_3)(\eta^6$-$C_6Me_6)$],[10] likely due to the *trans* influence of the alkynyl group. The formation of complexes **6** from **5** shows that protonation of the Ru–alkynyl moiety can be achieved by the NH_4^+ cation and takes place with elimination of free terminal alkyne to generate a vacant coordination site for ammonia. It suggests that the resulting complex containing *trans* vinylidene and alkynyl ligands bonded to the Ru(dppe)$_2$ moiety is not stable or that protonation eventually takes place at the C-1, or at the ruthenium atom followed by reductive elimination. The coordination of ammonia to the 16-electron intermediate $[Ru(C{\equiv}CR)(dppe)_2]^+$ resulting from the dissociation of the Ru–Cl bond of complexes **4**, was checked by the reaction of derivatives **4a–c** simply with NH_4PF_6 in a polar solvent (CH_2Cl_2) which leads to very slow formation of the complexes **6a–c**. This reaction cannot be performed with $[RuCl(C{\equiv}CR)(dppm)_2]$ complexes.

The evidence that the Ru–Cl bond complex **4a** was labile led us to attempt the generation of the first allenylidene alkynyl metal complex, as it is known that the formation of the stable allenylidene $[Ru{=}C{=}C{=}CPh_2(Cl)(dppm)_2]^+$ cation was possible by reaction of $[RuCl_2(dppm)_2]$ with $HC{\equiv}CCPh_2OH$.[2] The reaction of **3a** with 2 equiv. of Et_3N, $NaPF_6$ and $HC{\equiv}CCPh_2OH$ led to the formation of the deep-blue complex **7a** obtained in 60% yield (Scheme 2). It shows a strong IR absorption at 1921 cm^{-1} ($\nu_{C=C=C}$) and a medium one at 2065 cm^{-1} ($\nu_{C{\equiv}C}$). The ^{13}C NMR spectrum shows the characteristic resonances for both allenylidene and alkynyl ligands [δ 316.58 (quint, Ru=C, $^2J_{PC}$ 14 Hz), 213.21 (quint, Ru=C=C, $^3J_{PC}$ 2 Hz), 162.31 (s, $=CPh_2$), 120.05 (quint, Ru–C≡, $^2J_{PC}$ 18 Hz)].

The novel allenylidene alkynyl derivative **7a** is a model for carbon–carbon bond formation by *trans–cis* isomerization of the hydrocarbon ligands.

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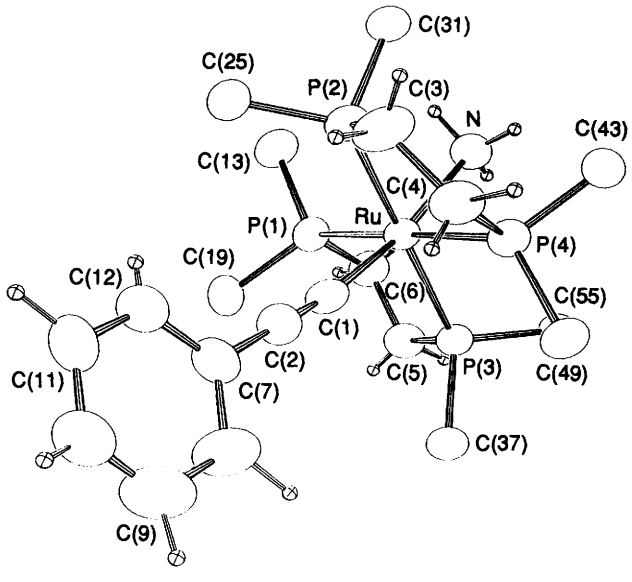

Fig. 1 Molecular structure of cation $[H_3NRuC{\equiv}CPh(PH_2PCH_2CH_2PPh_2)_2]^+$ **6a** (ORTEP view). For clarity the C–H atoms of phenyl groups have been omitted. Selected bond distances (Å) and angles (°): Ru–P(1) 2.401(1), Ru–P(2) 2.347(1), Ru–P(3) 2.385(1), Ru–P(4) 2.347(1), Ru–N 2.215(5),Ru–C(1) 2.014(5), C(1)–C(2) 1.187(7), C(2)–C(7) 1.441(7); C(1)–Ru–N 169.1(2), Ru–C(1)–C(2) 168.9(5), C(1)–C(2)–C(7) 179.1(5).

Footnote

† *Crystal data*: $C_{60}H_{56}NP_4Ru$, PF_6 **6a**: M_r = 1161.05, monoclinic, *Cc*, *a* = 14.345(7), *b* = 22.079(3), *c* = 17.857 (4) Å, β = 104.00(3)°, *V* = 5488(2) $Å^{-3}$, *Z* = 4, D_x = 1.405 Mg m^{-3}, λ(Mo-Kα) = 0.70926 Å, μ = 4.81 cm^{-1}, *F*(000) = 2384, *T* = 294 K, final *R* = 0.031 for 5134 observations. The sample (0.30 × 0.45 × 0.55 mm) was studied on an automatic CAD4 Enraf-Nonius diffractometer with graphite monochromatised Mo-Kα radiation. The cell parameters were obtained by fitting a set of 25 high-θ reflections. The data collection ($2\theta_{max}$ = 54°, scan $\omega/2\theta$ = 1, t_{max} = 60 s, range *hkl*: *h* 0.18, *k* 0.28, *l* −22.22, intensity controls without appreciable decay (0.1%) gives 6396 reflections from which 5134 were independent (R_{int} = 0.014) with $I > 2\sigma(I)$. After Lorenz and polarization corrections the structure was solved with direct methods which revealed the Ru and P atoms. The remaining non-hydrogen atoms of the structure were found after successive scale factor refinements and Fourier differences. After isotropic (*R* = 0.090) and then anisotropic refinement (*R* = 0.07), many hydrogen atoms (in particular hydrogen atoms of nitrogen) were found with a Fourier difference (beween 0.21 and 0.09 e $Å^{-3}$). The whole structure was refined by the full-matrix least-square technique (use of *F* magnitude; *x*, *y*, *z*, β_{ij} for Ru, P, F, N and C atoms and *x*, *y*, *z* for H atoms; 819 variables and 5134 observations. $\omega = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with the resulting *R* = 0.033, *Rw* = 0.031 and *Sw* = 1.1 (residual $\Delta\rho \leqslant 0.12$ e $Å^{-3}$). Atomic scattering factors from International Tables for X-ray crystallography (1974). All the calculations were performed on a Digital Micro VAX 3100 Computer with the MolEN package (Enraf-Nonius, 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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