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# Unexpected coupling between an η⁵-indenyl ligand and alkenyl-vinylidene fragments: synthesis of unprecedented (η⁶-indene)ruthenium(II) metallacycles†

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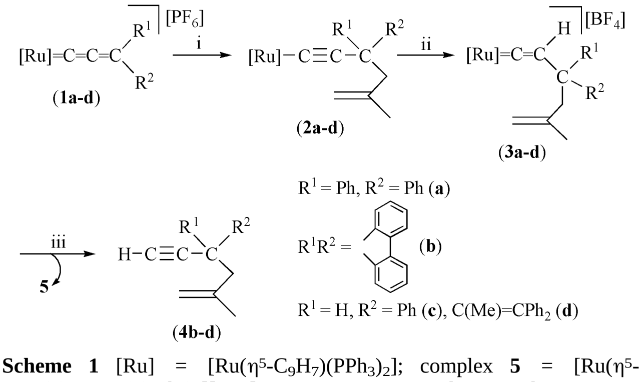
**Vinylidene complexes [Ru{=C=C(H)CR$^1$R$^2$CH$_2$C(Me)=CH$_2$}(η$^5$-C$_9$H$_7$)(PPh$_3$)$_2$][BF$_4$] undergo an intramolecular coupling between the alkenyl-vinylidene fragment and the η$^5$-indenyl ligand to afford indene-metallacyclic compounds (6a,b) in which the resulting functionalised indene group is η$^6$-coordinated to the metal.**

The reactivity of transition-metal allenylidene complexes [M]=C=C=CR$_2$ has attracted a great deal of attention in the last decade[1] and important applications in organic synthesis are now emerging.[2] In this context, we have recently reported an easy entry to terminal 1,5-enynes HC≡CCR$^1$R$^2$CH$_2$CH=CH$_2$ starting from indenyl-ruthenium(II) allenylidenes [Ru(=C=C=CR$^1$R$^2$)-(η$^5$–C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] and allylmagnesium bromide.[3] The following processes are involved in this synthetic route: (i) regioselective nucleophilic addition of the Grignard reagent at the electrophilic C$_\gamma$ atom of the allenylidene chain to give σ-alkynyl derivatives [Ru(C≡CCR$^1$R$^2$CH$_2$CH=CH$_2$)(η$^5$-C$_9$H$_7$)-(PPh$_3$)$_2$], (ii) selective C$_\beta$ protonation of these σ-alkynyl complexes to afford the corresponding alkenyl-vinylidene derivatives [Ru{=C=C(H)CR$^1$R$^2$CH$_2$CH=CH$_2$}(η$^5$-C$_9$H$_7$)-(PPh$_3$)$_2$]$^+$, and finally (iii) demetalation of the vinylidene complexes in refluxing acetonitrile to give the free 1,5-enynes, recovering the metal fragment as the acetonitrile solvate [Ru(η$^5$-C$_9$H$_7$)(N≡CMe)(PPh$_3$)$_2$]$^+$.

In order to investigate the scope of this synthetic approach, the reactivity of [Ru(=C=C=CR$^1$R$^2$)(η$^5$-C$_9$H$_7$)(PPh$_3$)$_2$][PF$_6$] (**1a–d**)[4] towards 2-methylallylmagnesium chloride was explored. Thus, following the same synthetic protocol used in our previous report,[3] σ-alkynyl derivatives **2a–d** and alkenyl-vinylidene complexes **3a–d** were prepared in 77–86% and 91–95% yields, respectively (Scheme 1).‡

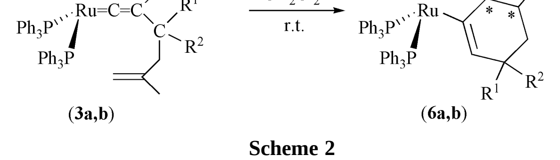


**Scheme 1** [Ru] = [Ru(η$^5$-C$_9$H$_7$)(PPh$_3$)$_2$]; complex **5** = [Ru(η$^5$-C$_9$H$_7$)(N≡CMe)(PPh$_3$)$_2$][BF$_4$]. *Reagents and conditions*: i, CH$_2$=C(Me)CH$_2$MgCl (1 equiv.), THF, −20 °C; ii, HBF$_4$ (1 equiv.), Et$_2$O, −20 °C; iii, MeC≡N, reflux.

Demetalation of vinylidenes **3a–d** in refluxing acetonitrile proceeds as expected (except for **3a**), yielding the novel 1,5-enynes **4b–d** (90–94% isolated yields) and the nitrile complex [Ru(η$^5$-C$_9$H$_7$)(N≡CMe)(PPh$_3$)$_2$][BF$_4$] (**5**) quantitatively (Scheme 1).‡ All attempts to prepare HC≡CCPh$_2$CH$_2$C(Me)=CH$_2$ by heating acetonitrile solutions of **3a** failed, resulting instead, besides free PPh$_3$, in complicated mixtures of uncharacterized species. However, stirring a solution of **3a** in acetonitrile or dichloromethane at room temperature gives in *ca.* 3 h the unprecedented cyclometalated (η$^6$-indene)ruthenium(II) complex **6a**, isolated from the reaction mixture as an air-stable orange solid (87% yield) (Scheme 2).§ Similarly, vinylidene derivatives **3b–d** give also analogous metallacycles although longer reaction times are required (*ca.* 72 h), and only complex **6b** is obtained with analytical purity (85% yield) (Scheme 2).§ Complexes **6a,b** formally result from the coupling of the terminal carbon atom of the alkenyl group with the η$^5$-indenyl ligand after a ring closure of the alkenyl-vinylidene moiety. Apparently, the competitive η$^1$-vinylidene–η$^2$-alkyne tautomerization, a key step in the demetalation process,[3] is a faster process for vinylidenes **3b–d** allowing the isolation of the terminal 1,5-enynes **4b–d**.

Analytical and spectroscopic data of complexes **6a,b** support the proposed formulation.§ Note that formation of these metallacycles involves the generation of three stereogenic centers (Scheme 2). $^{31}$P-{$^1$H} NMR spectroscopy reveals that the reactions proceed stereoselectively since only one diastereoisomer is observed, the spectra consisting of two doublet resonances in accordance with the nonequivalence of the phosphorus nuclei. $^1$H and $^{13}$C-{$^1$H} NMR spectra are also in agreement with the proposed structures. In particular, the alkenyl Ru–C=CH carbons resonate at *ca.* $\delta_C$ 150 (dd, $^2J$(CP) = 9.4–16.9 Hz) and 138 (s) ppm, respectively.[5]

In addition, the structure of **6b** has been determined by a single-crystal X-ray diffraction study (Fig. 1).¶ As expected, the two enantiomers are present in the unit cell displaying $R_{C1}S_{C10}S_{C11}$ and $S_{C1}R_{C10}R_{C11}$ configurations (two molecules for each one; only one of the molecules displaying $R_{C1}S_{C10}S_{C11}$ configuration is shown in Fig. 1). The molecular structure shows the typical pseudooctahedral three-legged piano-stool coordination around the ruthenium atom, which is bonded to the functionalised indene unit acting as a η$^6$-ligand, the phosphorus atoms from PPh$_3$, and a 1-cyclohexenyl ring (the bond length Ru–C(16) of 2.138(5) Å is consistent with a ruthenium–carbon



**Scheme 2**

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b212406h/

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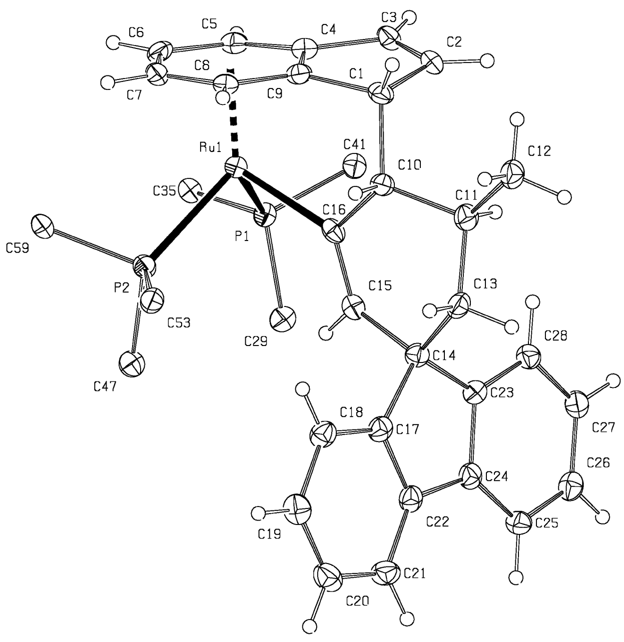

**Fig. 1** Molecular structure and numbering scheme of **6b** (only one of the independent molecules is shown; bond lengths and angles are only for this molecule). Tetrafluoroborate anion, THF molecules and phenyl groups of the $PPh_3$ ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru–C* 1.814(16); Ru–P(1) 2.3755(13); Ru–P(2) 2.3736(13); Ru–C(16) 2.138(5); C(1)–C(2) 1.516(7); C(2)–C(3) 1.327(7); C(1)–C(10) 1.559(16); C(10)–C(11) 1.530(7); C(10)–C(16) 1.547(7); C(11)–C(13) 1.530(7); C(13)–C(14) 1.531(7); C(14)–C(15) 1.528(7); C(15)–C(16) 1.349(6); C*–Ru–P(1) 123.84(16); C*–Ru–P(2) 125.81(17); C*–Ru–C(16) 116.07(21); P(1)–Ru–P(2) 98.48(5); P(1)–Ru–C(16) 92.02(13); P(2)–Ru–C(16) 91.81(13). C* = centroid of C(4), C(5), C(6), C(7), C(8) and C(9).

single bond). The C(2)–C(3) and C(15)–C(16) distances (1.327(7) and 1.349(6) Å, respectively) show the expected values for a double carbon–carbon bond.

The most remarkable feature of this coupling is the generation of a functionalised $\eta^6$-coordinated indene derivative from a $\eta^5$-indenyl complex. Although $\eta^5 \rightarrow \eta^6$ haptotropic rearrangements have been reported as the result of protonation of $\eta^5$-indenyl complexes,[6] as far as we know these are the first rearrangements mediated by a C–C coupling. We note that the related alkenyl-vinylidene derivative $[Ru\{=C=C(H)CPh_2CH_2CH=CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$[3] does not rearrange in solution, to afford the corresponding ($\eta^6$-indene)ruthenium(II) metallacycle, even in refluxing dichloromethane. This fact seems to indicate that electron-rich alkenyl units, *i.e.* $C(CH_3)=CH_2$, are required in this coupling process.

Further studies concerning the scope and mechanism[7,8] of this unusual carbocyclization, as well as reactivity studies on the resulting metallacycles, are now under active investigation.

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## Notes and references

‡ Compounds **2–4a–d** have been characterized by NMR spectroscopy and elemental analyses or HRMS. See ESI.

§ A solution of the corresponding vinylidene complex $[Ru\{=C=C(H)CR^1R^2CH_2C(Me)=CH_2\}(\eta^5\text{-}C_9H_7)(PPh_3)_2][BF_4]$ (**3a,b**; 1 mmol) in dichloromethane (30 $cm^3$) was stirred at room temperature for 3 (**6a**) or 72 (**6b**) h. The solution was then evaporated to dryness and the resulting solid residue washed with diethyl ether (3 × 10 $cm^3$) and vacuum-dried. *Selected spectroscopic data (numbering for protons and carbons follows the crystallographic scheme shown in Fig. 1):* **6a**: $\delta_P$ ($CD_2Cl_2$) 28.66 and 34.40 (d, $^2J$(PP) = 54.0); $\delta_H$ ($CD_2Cl_2$) 1.09 (d, 3 H, $J$(HH) = 6.3, H-12), 1.72 (m, 1 H, H-13), 2.03 (dd, 1 H, $J$(HH) = 12.5 and 12.5, H-13), 3.20 (m, 1 H, H-11), 3.93 (m, 1 H, H-10), 4.01 (m, 1 H, H-1), 4.57 (br, 1 H, H-15), 5.10 (br, 1 H, H-3), 5.57, 5.93, 6.01 and 6.20 (br, 1 H each, H-5, H-6, H-7 and H-8), 6.60 (br, 1H, H-2), 6.71–7.41 (m, 40 H, Ph); $\delta_C$ ($CD_2Cl_2$) 22.60 (s, C-12), 35.78 (s, C-11), 43.51 (s, C-13), 51.13 (s, C-1), 52.80 (s, C-14), 80.78 (s, C-10), 86.90, 93.50, 95.57 and 98.32 (s, C-5, C-6, C-7 and C-8), 101.26 (s, C-4 or C-9), 111.63 (d, $^2J$(CP) = 7.7, C-4 or C-9), 125.95–150.31 (m, Ph), 129.99 and 144.66 (s, C-2 and C-3), 137.91 (s, C-15), 153.95 (dd, $^2J$(CP) = 16.9 and 11.7, C-16). **6b**: $\delta_P$ ($CD_2Cl_2$) 27.75 and 29.48 (d, $^2J$(PP) = 60.2); $\delta_H$ ($CD_2Cl_2$) 1.31 (d, 3 H, $J$(HH) = 6.2, H-12), 1.72 (m, 1 H, H-13), 1.99 (dd, 1 H, $J$(HH) = 13.3 and 13.3, H-13), 2.73 (m, 1 H, H-11), 3.90 (m, 1 H, H-10), 4.04 (m, 1 H, H-1), 4.89 (br, 1 H, H-15), 5.00 (br, 1 H, H-3), 5.44, 5.52, 5.73 and 5.80 (br, 1 H each, H-5, H-6, H-7 and H-8), 6.41–7.97 (m, 38 H, Ph and $C_{12}H_8$), 6.90 (br, 1H, H-2); $\delta_C$ ($CD_2Cl_2$) 22.90 (s, C-12), 38.17 (s, C-11), 42.67 (s, C-13), 53.61 (s, C-1), 55.21 (s, C-14), 77.59 (s, C-10), 82.90, 94.94, 96.03 and 99.21 (s, C-5, C-6, C-7 and C-8), 103.66 (s, C-4 or C-9), 107.27 (d, $^2J$(CP) = 9.4, C-4 or C-9), 120.36–152.86 (m, Ph and $C_{12}H_8$), 131.00 and 142.73 (s, C-2 and C-3), 138.10 (s, C-15), 148.23 (dd, $^2J$(CP) = 15.7 and 9.4, C-16).

¶ Crystal data for **6b**: $C_{64}H_{53}BF_4P_2Ru\cdot 3/2THF$, $M$ = 1180.04, orange prism (0.175 × 0.15 × 0.075 mm), triclinic, $P\bar{1}$, $a$ = 14.7232(5), $b$ = 18.8325(7), $c$ = 21.3164(9) Å, $\alpha$ = 70.118(2), $\beta$ = 80.999(2), $\gamma$ = 83.676(2)°, $V$ = 5479.4(4) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.430 g $cm^{-3}$, $\mu$(Cu-K$\alpha$) = 3.364 $mm^{-1}$, Nonius Kappa CCD diffractometer, Cu-K$\alpha$ radiation ($\lambda$ = 1.54184 Å). 158352 reflections collected, 20043 unique (12474 with $I > 2\sigma(I)$). $R_1$ = 0.0564; $wR_2$ = 0.1298 both for $I > 2\sigma(I)$. CCDC 199722. See http://www.rsc.org/suppdata/cc/b2/b212406h/ for crystallographic data in CIF or other electronic format.

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5 These chemical shifts are typical of alkenyl-ruthenium(II) derivatives. See for example: K. Bieger, J. Díez, M. P. Gamasa, J. Gimeno, M. Pavlišta, Y. Rodríguez-Álvarez, S. García-Granda and R. Santiago-García, *Eur. J. Inorg. Chem.*, 2002, 1647.

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7 (*a*) No intermediates could be detected by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy (*b*) transformation of **3a,b** into **6a,b** proceeds in the presence of the radical-scavenger 2,6-di-*tert*-butyl-4-methylphenol, discarding the involvement of free radicals in this coupling process.

8 Although the exact mechanism of this reaction is still unknown, the following processes could be involved: (*a*) intramolecular [2 + 2] cycloaddition between the two C=C double bonds of the alkenyl-vinylidene group. A process of this type has been recently reported: P. Álvarez, E. Lastra, J. Gimeno, M. Bassetti and L. R. Falvello, *J. Am. Chem. Soc.*, 2003, **125**, 2386; (*b*) direct carbocyclization of the electron-rich double bond at the $C_\alpha$ of the vinylidene unit. A process of this type has been proposed in the catalytic cyclization of dienyl alkynes: C. A. Merlic and M. E. Pauly, *J. Am. Chem. Soc.*, 1996, **118**, 11319; (*c*) $\eta^5$ to $\eta^3$ slippage of the indenyl ligand: M. J. Calhorda and L. F. Veiros, *Coord. Chem. Rev.*, 1999, **185–186**, 37; V. Cadierno, J. Díez, M. P. Gamasa, J. Gimeno and E. Lastra, *Coord. Chem. Rev.*, 1999, **193–195**, 147; M. J. Calhorda, C. C. Romao and L. F. Veiros, *Chem. Eur. J.*, 2002, **8**, 868.