

Unexpected coupling between an η^5 -indenyl ligand and alkenyl-vinylidene fragments: synthesis of unprecedented (η^6 -indene)ruthenium(II) metallacycles†

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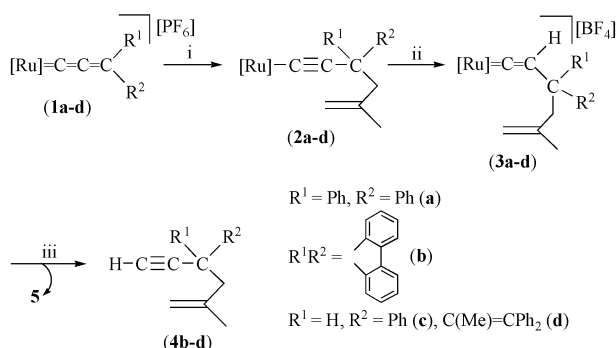
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Vinylidene complexes $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{CR}^1\text{R}^2\text{CH}_2\text{C}(\text{Me})=\text{CH}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{BF}_4]$ undergo an intramolecular coupling between the alkenyl-vinylidene 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 $[\text{M}]=\text{C}=\text{C}=\text{CR}_2$ has attracted a great deal of attention in the last decade¹ 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 $\text{HC}\equiv\text{CCR}^1\text{R}^2\text{CH}_2\text{CH}=\text{CH}_2$ starting from indenyl-ruthenium(II) allenylidenes $[\text{Ru}(\text{C}=\text{C}=\text{CR}^1\text{R}^2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ 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_γ atom of the allenylidene chain to give σ -alkynyl derivatives $[\text{Ru}(\text{C}\equiv\text{CCR}^1\text{R}^2\text{CH}_2\text{CH}=\text{CH}_2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$, (ii) selective C_β protonation of these σ -alkynyl complexes to afford the corresponding alkenyl-vinylidene derivatives $[\text{Ru}\{\text{C}=\text{C}(\text{H})\text{CR}^1\text{R}^2\text{CH}_2\text{CH}=\text{CH}_2\}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]^+$, 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 $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{N}\equiv\text{CMe})(\text{PPh}_3)_2]^+$.

In order to investigate the scope of this synthetic approach, the reactivity of $[\text{Ru}(\text{C}=\text{C}=\text{CR}^1\text{R}^2)(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2][\text{PF}_6]$ (**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).[‡]



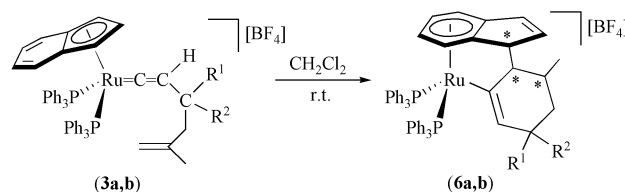
Scheme 1 $[\text{Ru}] = [\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{PPh}_3)_2]$; complex **5** = $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{N}\equiv\text{CMe})(\text{PPh}_3)_2][\text{BF}_4]$. Reagents and conditions: i, $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\text{MgCl}$ (1 equiv.), THF, $-20\text{ }^\circ\text{C}$; ii, HBF_4 (1 equiv.), Et_2O , $-20\text{ }^\circ\text{C}$; iii, $\text{MeC}\equiv\text{N}$, reflux.

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

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 $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)(\text{N}\equiv\text{CMe})(\text{PPh}_3)_2][\text{BF}_4]$ (**5**) quantitatively (Scheme 1).[‡] All attempts to prepare $\text{HC}\equiv\text{CCPh}_2\text{CH}_2\text{C}(\text{Me})=\text{CH}_2$ 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). ³¹P-¹H 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. ¹H and ¹³C-¹H NMR spectra are also in agreement with the proposed structures. In particular, the alkenyl $\text{Ru}-\text{C}=\text{CH}$ carbons resonate at ca. δ_{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 $R_{\text{C}1}\text{S}_{\text{C}10}\text{S}_{\text{C}11}$ and $\text{S}_{\text{C}1}\text{R}_{\text{C}10}\text{R}_{\text{C}11}$ configurations (two molecules for each one; only one of the molecules displaying $R_{\text{C}1}\text{S}_{\text{C}10}\text{S}_{\text{C}11}$ 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 $\text{Ru}-\text{C}(16)$ of 2.138(5) Å is consistent with a ruthenium–carbon



Scheme 2

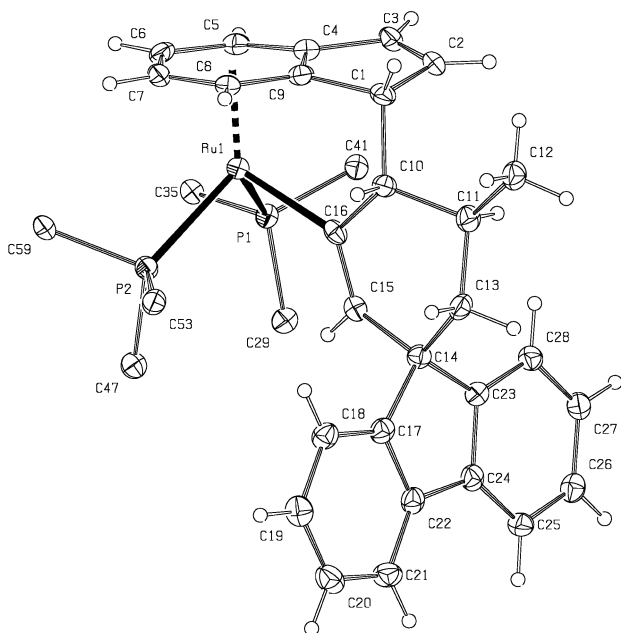


Fig. 1 Molecular structure and numbering scheme of **6b** (only one of the independent molecules is shown; bond lengths and angles are only for this molecule). Tetrafluoroborate anion, THF molecules and phenyl groups of the PPh₃ ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): 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 η^6 -coordinated indene derivative from a η^5 -indenyl complex. Although $\eta^5 \rightarrow \eta^6$ haptotropic rearrangements have been reported as the result of protonation of η^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)CPh₂CH₂CH=CH₂}(η^5 -C₉H₇)(PPh₃)₂][BF₄]³ does not rearrange in solution, to afford the corresponding (η^6 -indene)ruthenium(II) metallacycle, even in refluxing dichloromethane. This fact seems to indicate that electron-rich alkenyl units, *i.e.* C(CH₃)=CH₂, 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)CR¹R²CH₂C(Me)=CH₂}(η^5 -C₉H₇)(PPh₃)₂][BF₄] (**3a,b**; 1 mmol) in dichloromethane (30 cm³) 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 cm³) and vacuum-dried. Selected spectroscopic data (numbering for protons and carbons follows the crystallographic scheme shown in Fig. 1): **6a**: δ_P (CD₂Cl₂) 28.66 and 34.40 (d, ²J(PP) = 54.0); δ_H (CD₂Cl₂) 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); δ_C (CD₂Cl₂) 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**: δ_P (CD₂Cl₂) 27.75 and 29.48 (d, ²J(PP) = 60.2); δ_H (CD₂Cl₂) 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 C₁₂H₈), 6.90 (br, 1H, H-2); δ_C (CD₂Cl₂) 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 C₁₂H₈), 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**: C₆₄H₅₃BF₄P₂Ru·3/2THF, *M* = 1180.04, orange prism (0.175 × 0.15 × 0.075 mm), triclinic, *P*1̄, *a* = 14.7232(5), *b* = 18.8325(7), *c* = 21.3164(9) Å, α = 70.118(2), β = 80.999(2), γ = 83.676(2)°, *V* = 5479.4(4) Å³, *Z* = 4, *D*_{calc} = 1.430 g cm⁻³, μ (Cu–K α) = 3.364 mm⁻¹, Nonius Kappa CCD diffractometer, Cu–K α radiation (λ = 1.54184 Å), 158352 reflections collected, 20043 unique (12474 with *I* > 2 σ (*I*)). *R*₁ = 0.0564; *wR*₂ = 0.1298 both for *I* > 2 σ (*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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- (a) No intermediates could be detected by ³¹P-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.
- 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 α 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) η^5 to η^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.