

## A New Route to Vinylcarbene Metal Complexes in One Step from 2-Propyn-1-ols and Arene Ruthenium(II) Derivatives

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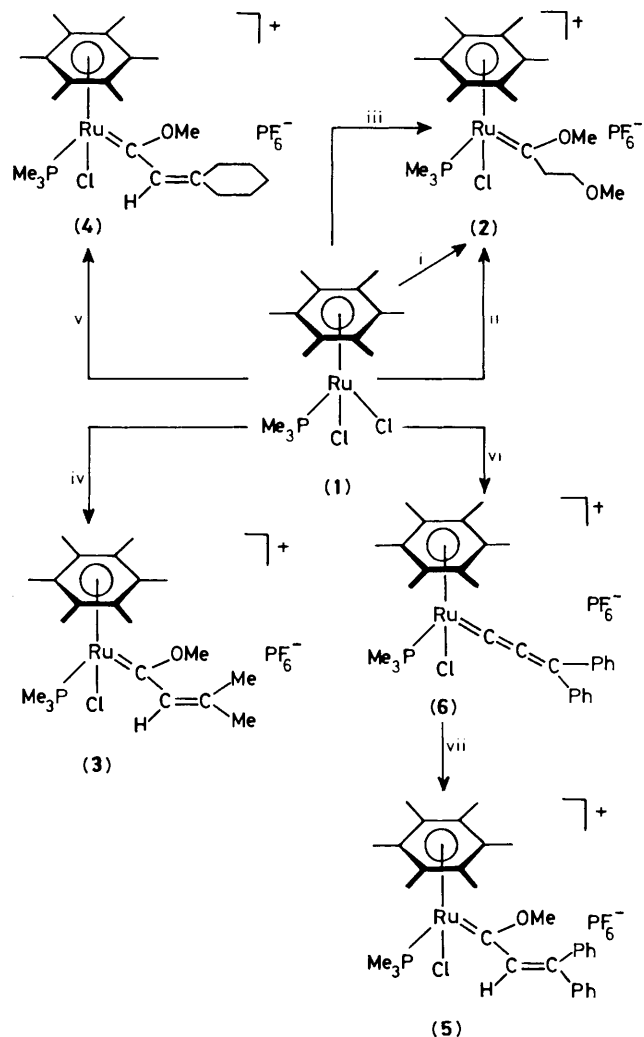
Complex  $(C_6Me_6)RuCl_2(PMe_3)$  (**1**) reacts at room temperature with  $HC\equiv CCR_2OH$  and  $NaPF_6$  in methanol to produce either  $[(C_6Me_6)Ru\{=C(OMe)CH_2CR_2OMe\}Cl(PMe_3)]PF_6$  ( $R = H$ ), (**2**) or  $[(C_6Me_6)Ru\{=C(OMe)CH=CR_2\}]PF_6$  ( $R \neq H$ ), (**3**)—(**5**) derivatives *via* an allenylidene-ruthenium intermediate, electrochemical studies of (**3**)—(**5**) show a reversible  $Ru^{III}/Ru^{II}$  oxidation process and irreversible oxidation of the double bond.

Vinylcarbene metal derivatives show potential as metal containing unsaturated substrates. They offer dienophile activation of the carbon-carbon double bond in cycloaddition reactions,<sup>1</sup> provide a route to vinylcyclopropane derivatives by coupling reactions with alkenes,<sup>2,3</sup> and are intermediates in alkyne polymerisation.<sup>4,5</sup> Several methods have been elaborated for the preparation of vinylcarbene-metal derivatives. They involve either the addition of aldehydes or ketones to deprotonated carbene metal complexes,<sup>6,7</sup> the addition of vinyl-lithium to metal carbonyl complexes followed by alkylation,<sup>8</sup> the protonation of dienylnmetal derivatives,<sup>2</sup> the hydroxide elimination of 3-hydroxy, prop-2-enyl metal derivatives<sup>3</sup> or the alkylation of vinylacyl-metal compounds.<sup>9</sup> Each of these multi-step reactions has been carried out with metal carbonyl complexes. A vinylcarbene derivative of early transition metal has been obtained by coupling of an alkyne with an alkylidene-tantalum complex.<sup>10</sup> Here we report our initial results concerning the preparation of the first vinylcarbene  $d^6$  metal complexes which do not contain carbonyl ligands, in one step by activation of 2-propyn-1-ols with arene ruthenium(II) derivatives. This reaction supports allenylidene-ruthenium intermediates.

Arene  $RuCl_2(PR_3)_2$  complexes were shown to be efficient catalyst precursors for the addition of ammonium carbamates and carboxylic acids to 2-propyn-1-ols.<sup>11</sup> In an attempt to gain insight into the reaction we have investigated the stoichiometric interaction between  $(\eta^6-C_6Me_6)RuCl_2(PMe_3)$  (**1**) and 2-propyn-1-ol derivatives. Complex (**1**) was treated in methanol with an excess (2.5 equiv.) of 2-propyn-1-ol in the presence of 1 equiv. of  $NaPF_6$ . After 10 min of reaction at room temperature red crystals of (**2**) were isolated (74%

yield).† The same complex (**2**) was also formed by a similar

† Satisfactory elemental analyses were obtained for (**2**)—(**5**). Selected spectroscopic data for: (**2**): I.r. (Nujol) 1280 (w,  $\nu_{C-O}$ ); 840 (s,  $\nu_{P-F}$ )  $cm^{-1}$ ;  $^{31}P\{^1H\}$  n.m.r. (32.38 MHz,  $CD_3COCD_3$ , 309 K)  $\delta$  8.8 (s,  $PMe_3$ ), -145.2 (sept,  $PF_6^-$ );  $^1H$  n.m.r. (300.13 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  4.60 (s, 3H,  $MeOC=$ Ru), 3.77 and 3.71 (AB q, 2H,  $=C-CH_2$ ,  $^2J_{HH}$  13 Hz), 3.86 and 3.38 (AB q, 2H,  $-CH_2-O$ ,  $^2J_{HH}$  24 Hz), 3.29 (s, 3H,  $CH_2-OMe$ ), 2.10 (s, 18H,  $C_6Me_6$ ), 1.37 (d, 9H,  $PMe_3$ ,  $^2J_{PH}$  10.7 Hz);  $^{13}C\{^1H\}$  n.m.r. (75.46 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  325.8 (d,  $Ru=C$ ,  $^2J_{PC}$  21.2 Hz), 107.9 (s,  $C_6Me_6$ ), 69.5 (s,  $-CH_2-O$ ), 67.7 (s,  $=COMe$ ), 58.9 (s,  $CH_2OMe$ ), 51.1 (s,  $=C-CH_2-$ ), 16.5 (s,  $C_6Me_6$ ), 15.7 (d,  $PMe_3$ ,  $^2J_{PC}$  32.5 Hz). (**3**): I.r. (Nujol) 1595 (w,  $\nu_{C=C}$ ); 1280 (w,  $\nu_{C-O}$ );  $^{31}P\{^1H\}$  n.m.r. (121.49 MHz,  $CD_2Cl_2$ , 213 K)  $\delta$  7.7 (s,  $PMe_3$ )  $\delta$  -143.8 (sept,  $PF_6^-$ );  $^1H$  n.m.r. (300.13 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  6.68 (s, 1H,  $HC=$ ), 4.73 (s, 3H,  $-OMe$ ), 1.94 (s, 3H,  $=CMe$ ), 1.90 (s, 3H,  $=CMe$ );  $^{13}C\{^1H\}$  n.m.r. (75.46 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  306.9 (d,  $Ru=C$ ,  $^2J_{PC}$  18.9 Hz), 149.4 (s,  $=C-Me$ ), 138.7 (d,  $=CH$ ,  $^2J_{PC}$  6.0 Hz), 68.7 (s,  $OMe$ ), 28.3 (s,  $=CMe$ ), 23.5 (s,  $=CMe$ ). (**4**): I.r. (Nujol) 1590 (w,  $\nu_{C=C}$ ), 1280 (w,  $\nu_{C-O}$ );  $^{31}P\{^1H\}$  n.m.r. (121.496 MHz,  $CD_2Cl_2$ , 213 K)  $\delta$  7.35 (s,  $PMe_3$ ), -143.50 (sept.,  $PF_6^-$ );  $^1H$  n.m.r. (300.134 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  6.54 (s, 1H,  $HC=$ ), 4.65 (s, 3H,  $OMe$ ), 1.71—1.46 [m, 10H,  $(CH_2)_5$ ];  $^{13}C\{^1H\}$  n.m.r. (75.469 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  310.15 (d,  $Ru=C$ ,  $^2J_{PC}$  22.44 Hz), 155.93 [s,  $=C(CH_2)_5$ ], 134.74 (s,  $HC=$ ), 68.84 (s,  $OMe$ ), 33.36, 29.30, 28.16, 26.16 [s,  $(CH_2)_5$ ]. (**5**): I.r. (Nujol) 1590 (w,  $\nu_{C=C}$ ), 1280 (w,  $\nu_{C-O}$ );  $^{31}P\{^1H\}$  n.m.r. (121.49 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  5.2 (s,  $PMe_3$ ),  $\delta$  -143.5 (sept.,  $PF_6^-$ );  $^1H$  n.m.r. (300.13 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  7.50 (s, 1H,  $HC=$ ), 7.35 (s, 10H,  $Ph_2$ ), 4.11 (s, 3H,  $OMe$ );  $^{13}C\{^1H\}$  n.m.r. (75.46 MHz,  $CD_2Cl_2$ , 297 K)  $\delta$  304.2 (d,  $Ru=C$ ,  $^2J_{PC}$  18.7 Hz), 147.7 (s,  $=CPh_2$ ), 140.2 (s,  $HC=$ ), 67.9 (s,  $OMe$ ). (**6**): I.r. (Nujol) 1940 (m,  $\nu_{C=C=C}$ ), 840 (s,  $\nu_{P-F}$   $cm^{-1}$ );  $^{31}P\{^1H\}$  n.m.r. (32.38 MHz,  $CD_2Cl_2$ , 309 K)  $\delta$  1.9 (s,  $PMe_3$ ), -144.5 (sept,  $PF_6^-$ );  $^1H$  n.m.r. (80 MHz,  $CD_2Cl_2$ , 309K)  $\delta$  7.3 (m, 10H,  $Ph$ ), 2.00 (s, 18H,  $C_6Me_6$ ), 1.4 (d, 9H,  $PMe_3$ ,  $^2J_{PH}$  10 Hz).

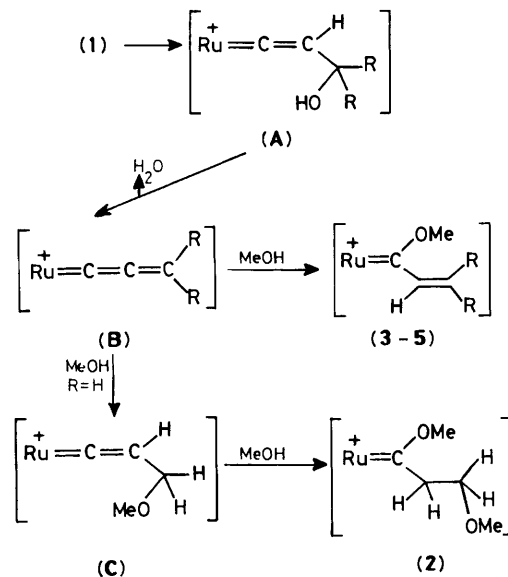


**Scheme 1.** Reagents and conditions (room temp. with  $\text{NaPF}_6$  in methanol): i,  $\text{HC}\equiv\text{CCH}_2\text{OH}$ , 10 min; ii,  $\text{HC}\equiv\text{CCH}_2\text{OMe}$ , 10 min; iii,  $\text{HC}\equiv\text{CCH}_2\text{Cl}$ , 10 min; iv,  $\text{HC}\equiv\text{C}(\text{Me})_2\text{OH}$ , 10 min; v,  $\text{HC}\equiv\text{C}(\text{C}_5\text{H}_{10})\text{OH}$ , 10 min; vi,  $\text{HC}\equiv\text{C}(\text{Ph})_2\text{OH}$ , 10 min; vii,  $\text{HC}\equiv\text{C}(\text{Ph})_2\text{OH}$ , 24 h.

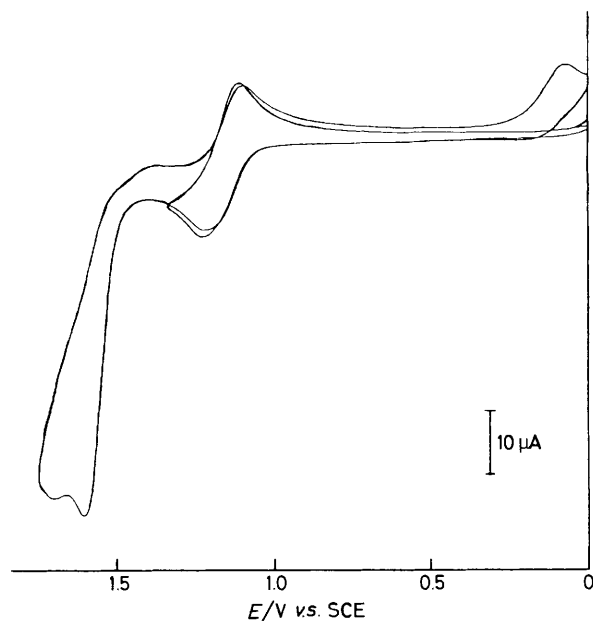
reaction of complex (1) with  $\text{HC}\equiv\text{CCH}_2\text{OMe}$  and  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  and isolated in 71 and 68% yields, respectively (Scheme 1).

Under similar conditions, complex (1) reacted with 1,1-dialkyl-2-propyn-1-ols  $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$  [ $\text{R} = \text{Me}$ ;  $\text{R}_2 = (\text{CH}_2)_5$ ] and after 15 min at room temperature the vinylcarbene derivatives (3)<sup>+</sup> and (4)<sup>+</sup> were obtained in 73 and 65% yields, respectively (Scheme 1). With 1,1-diphenyl-2-propyn-1-ol  $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ , the reaction was much slower. The solution colour became rapidly violet and then progressively red. After 24 h at room temperature the red vinylcarbene complex (5)<sup>+</sup> was isolated in 69% yield. When the reaction was quenched by addition of ether after 20 min. at 25 °C a violet precipitate was isolated (69%) which was identified as the allenylidene ruthenium intermediate (6). Each of these vinylcarbene ruthenium complexes (3)–(5) shows a low-field  $^{13}\text{C}$  n.m.r. doublet ( $\delta$  304–301) characteristic of carbene carbon, but at a slightly higher chemical shift than that of a non-conjugated ruthenium–carbene such as (2) ( $\delta$  325).

Of special interest are the electrochemical studies of vinylcarbene ruthenium complexes (3) and (5). Cyclic voltammetry in acetonitrile [0.1 M  $\text{Bu}_4\text{NPF}_6$ ; 200  $\text{mV s}^{-1}$ ] between 0



**Scheme 2**



**Figure 1.** Cyclic voltammogram of (5) in  $\text{CH}_3\text{CN}$  containing 0.1 M  $\text{Bu}_4\text{NPF}_6$ , at 0.2 V/s. (SCE = standard calomel electrode)

and +1.4 V vs standard calomel electrode (SCE) shows a quasi reversible wave at  $E_1 = +1.09$  V for (3) and +1.13 V for (5) (Figure 1), corresponding to the redox  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couple. The voltammograms recorded between 0 and +1.7 V show the appearance of a second anodic wave at  $E_p = +1.56$  V (3) and +1.57 V (5) which is totally irreversible. Moreover, a reverse scan shows a cathodic wave at  $E_p = +0.1$  V for (3) and (5) which is observed only when oxidation at +1.57 V is imposed before (Figure 1). This second process is consistent with the oxidation of the C=C double bond, followed by a chemical evolution into a species reducible at +0.1 V. Indeed, cyclic voltammograms of  $[(\text{C}_6\text{Me}_6)\text{RuCl}(\text{PMe}_3)(=\text{C}(\text{OMe})\text{CH}_2\text{R})]\text{PF}_6$  complexes show only one reversible wave between 1.0 and 1.2 V corresponding to the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  redox couple.<sup>12</sup>

The formation of complexes (2)—(5) from  $\text{HC}\equiv\text{CCR}_2\text{OH}$  derivatives can be explained *via* the vinylidene ruthenium (A) and then the allenylidene-ruthenium intermediate (B) which was observed only when R = Ph (6). The reaction of (1) with  $\text{HC}\equiv\text{CCH}_2\text{OCH}_3$  in  $\text{CD}_3\text{OD}$  led to the complex  $\{(\text{C}_6\text{Me}_6)\text{-Ru}[\text{C}(\text{OCD}_3)\text{CHDCH}_2\text{OCH}_3]\text{Cl}(\text{PMe}_3)\}\text{PF}_6$  (7), analogous to (2), showing that no exchange occurred between the methoxy group attached to C-3 and that of methanol. Thus, it is likely that from 2-propyn-1-ol itself addition of methanol gives first the intermediate (C) and then (2) (Scheme 2).

The reactions described here give evidence for the specific behaviour of (arene) $\text{RuCl}_2(\text{PR}_3)$  complexes as compared to the isoelectronic derivative  $(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{PMe}_3)_2$ . Selegue showed that the latter reacted with  $\text{HC}\equiv\text{CCR}_2\text{OH}$  derivatives to afford, when R = Me a bimetallic complex, and when R = Ph the corresponding allenylidene ruthenium complex without formation of the vinylcarbene ruthenium complex.<sup>13</sup>

The one-step formation of vinylcarbene arene ruthenium complexes (3)—(5) directly from the easily available  $\text{HC}\equiv\text{CCR}_2\text{OH}$  derivatives represents an advantage over the previous methods involving multi-step transformations and metal carbonyl derivatives.

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