Generation of γ -functionalized alkynyl ligands by migratory insertion of an allenylidene unit into a M–OR bond

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The hydroxyrhodium(1) complexes 2a,b, which are prepared from the corresponding chloro derivatives 1a,b and KOBu^t, react with acetic acid and phenol at room temperature to give the new acetato and phenolato metal compounds 3a,b and 4a,b almost quantitatively; subsequent treatment of 3a,b and 4a,b with CO leads to migratory insertion of the allenylidene unit into the Rh–OR bond to yield γ -functionalized alkynyl ligands.

Migratory insertion represents an important reaction pathway for organotransition metal complexes containing π -acceptor ligands such as CO, CNR, carbenes *etc.*¹ As far as *unsaturated* carbenes are concerned, we² as well as others³ have recently shown that in particular for d⁸ metal systems the barrier for migration of an alkyl, aryl, vinyl or alkynyl group R to vinylidenes C=CHR' is rather low and probably even lower in the case of allenylidenes C=C=CRR'.⁴ Here we report the first examples of formal insertion of an unsaturated carbene into metal–oxygen bonds which generates OR-functionalized alkynyl ligands.

The hydroxyrhodium(1) complexes **2a,b**, which were prepared from **1a,b** and KOBu^{t5} react with equimolar amounts of acetic acid or phenol to give the acetato and phenolato metal derivatives **3a,b** and **4a,b** in almost quantitative yield.[†] The IR and NMR spectra of the deeply coloured, comparatively airstable solids support the structural proposal shown in Scheme 1. The most characteristic features of the NMR spectroscopic data of **3a,b** and **4a,b** are the low-field signals at δ 245–251 (β -C) and 205–230 (α -C) which due to Rh–C and P–C coupling appear as doublets of triplets.[‡]



With regard to the mechanism of the migratory insertion process we attempted to prove the intramolecular pathway by a crossover experiment using **3a** and **4b** as starting materials. We observed, however, that before CO was passed through a solution of **3a** and **4b** in benzene a random exchange took place and a mixture of **3a**, **3b**, **4a** and **4b** was formed. Since on the other hand, the reaction of **4a** with CO in the *presence* of acetate cleanly yielded **6a** (and not a mixture of **5a** and **6a**), we believe that the formation of the alkynyl complexes **5a,b** and **6a,b** occurs intramolecularly and does not involve a heterolytic



Scheme 1 (L = PPrⁱ₃, **a**: R = Ph, **b**, R = o-C₆H₄Me). Reagents and conditions: i, KOBuⁱ, C₆H₆-BuⁱOH (10:1), 25 °C, 1 h, 80–85%; ii, MeCO₂H in benzene, 25 °C, 1 h, 90–95%; iii, PhOH in benzene, 25 °C, 10 min, 85–90%; iv, CO in benzene, 10 °C, 5 min, 90%; v, CO in benzene, 10 °C, 5 min, 80–90%.



Fig. 1 Molecular structure (ORTEP drawing) of **6a**. Selected bond distances (Å) and angles (°): Rh–P(1) 2.333(1), Rh–P(2) 2.331(1), Rh–C(1) 2.037(4), Rh–C(22) 1.830(4), C(1)–C(2) 1.205(5), C(2)–C(3) 1.478(5), C(22)–O(2) 1.147(5), C(3)–O(1) 1.442(5); P(1)–Rh–P(2) 168.80(4), P(1)–Rh–C(1) 89.4(1), P(1)–Rh–C(22) 90.3(1), P(2)–Rh–C(1) 90.8(1), P(2)–Rh–C(22) 90.3(1), C(1)–Rh–C(22) 175.8(2), Rh–C(22)–O(2) 178.1(5), Rh–C(1)–C(2) 175.8(4), C(1)–C(2)–C(3) 173.0(4), C(2)–C(3)–C(4) 107.8(3), C(2)–C(3)–C(1) 113.7(4), C(2)–C(3)–O(1) 111.6(3).

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cleavage of the Rh-OR bond. The most reasonable assumption is that on treatment of 3a,b and 4a,b with CO a five-coordinate intermediate, having the two phosphines in trans and the OR and the C=C=CRR' ligands in cis positions, is generated which after migration of the acetato or phenolato group to the terminal carbon atom of the allenylidene unit transforms into the isolated product. The formal 1,4-shift of the OR group may occur stepwise via an allenylmetal intermediate which rapidly rearranges to the alkynyl complex. It is important to note that in contrast to the reaction of *trans*-[Rh(OMe)(CO)(PPrⁱ₃)₂] with CO leading to trans-[Rh(CO₂Me)(CO)(PPri₃)₂],⁸ no insertion into the Rh-OPh bond takes place on treatment of 4a and 4b with carbon monoxide. Finally, it should be mentioned that the work by Dixneuf et al.9 has shown that uncharged oxygen donors such as ROH intermolecularly attack the α -carbon atom of the metal-bonded allenvlidenes thus generating alkoxy(vinyl)carbene ligands.

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Footnotes

† All new compounds gave satisfactory elemental analyses. 2a: green crystals, mp 138 °C (decomp.); 2b: green crystals, mp 119 °C (decomp.);
3a: green crystals, mp 93 °C (decomp.); 3b: green crystals, mp 156 °C (decomp.);
4a: black crystals, mp 127 °C (decomp.); 4b: black crystals, mp 123 °C (decomp.);
5a: yellow solid, mp 116 °C (decomp.); 5b: yellow solid, mp 116 °C (decomp.);
6a: yellow crystals, mp 124 °C;
6b: yellow crystals, mp 136 °C.

Inp 105 Cet ¹³C NMR spectroscopic data, in C_6D_6 (exemplified for complexes with R = Ph): **2a**, δ 247.4 [dt, J(RhC) 12.3, J(PC) 5.8 Hz, Rh=C=C], 221.8 [dt, J(RhC) 51.8, J(PC) 18.2 Hz, Rh=C], 129.7 (br s, Rh=C=C=C); **3a**, δ 245.0 [dt, J(RhC) 15.3, J(PC) 7.0 Hz, Rh=C=C], 204.8 [dt, J(RhC) 66.8, J(PC) 17.8 Hz, Rh=C], 175.9 (s, CO₂Me), 134.8 [t, br, J(PC) 2.5 Hz, Rh=C=C=C]; **4a**, δ 251.6 [dt, J(RhC) 14.6, J(PC) 5.7 Hz, Rh=C=C], 229.8 [dt, J(RhC) 59.1, J(PC) 18.4 Hz; Rh = C], 136.3 [t, J(PC) 2.2 Hz, Rh=C=C=C]; **5a**, δ 196.2 [dt, J(RhC) 59.1, J(PC) 14.0 Hz, RhCO], 125.5 [dt, J(RhC) 42.6, J(PC) 20.3 Hz, RhC=C], 114.8 [dt, J(RhC) 12.1, J(PC) 2.5 Hz, RhC=C]; **6a**, δ 196.2 [dt, J(RhC) 58.5, J(PC) 14.0 Hz, RhCO], 127.0 [dt, J(RhC) 43.1, J(PC) 20.6 Hz, RhC=C], 114.8 [dt, J(RhC) 12.2, J(PC) 3.0 Hz, RhC=C].

§ Crystal data for **6a**: crystals from acetone–acetonitrile (-10° C); C₄₀H₅₇O₂P₂Rh, M = 734.74; monoclinic, space group $P2_1/c$ (no.14), Z = 4, a = 12.819(4), b = 14.633(3), c = 21.020(7), $\beta = 92.36(2)^{\circ}$, U = 3940(2)Å³, $D_c = 1.239$ g cm⁻³, T = 293 K, max $2\theta = 48^{\circ}$, graphitemonochromated Mo-K α radiation ($\lambda = 0.70930$ Å). 6167 unique data were obtained and 4328 of these with $I > 2\sigma(I)$ were used in the refinement; R = 0.037, $R_w = 0.070$; GOF 1.16; residual electron density +0.400, -0.305e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/90.

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