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

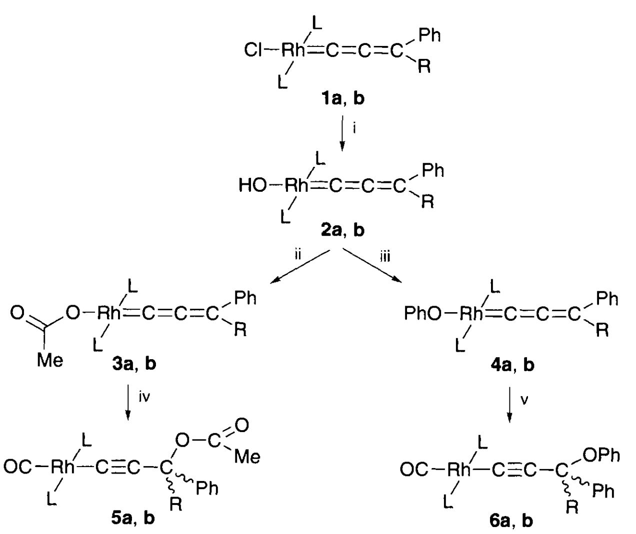
Helmut Werner,* Ralf Wiedemann, Matthias Laubender, Justin Wolf and Bettina Windmüller

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

The hydroxyrhodium(I) 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, we[2] as well as others[3] have recently shown that in particular for d^8 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(I) complexes **2a,b**, which were prepared from **1a,b** and KOBu^t[5] 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 air-stable 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.‡



Scheme 1 (L = PPr$^i_3$, **a**: R = Ph, **b**, R = *o*-C_6H_4Me). *Reagents and conditions*: i, KOBu^t, C_6H_6–Bu^{t}OH (10:1), 25 °C, 1 h, 80–85%; ii, $MeCO_2H$ 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%.

In contrast to **1a,b**, the new acetato and phenolato compounds **3a,b** and **4a,b** are highly reactive toward carbon monoxide. When CO was passed through a solution of **3a,b** or **4a,b** in benzene at 10 °C for 30 s, a characteristic change of colour from dark green or black to yellow occurred and, after removal of the solvent, yellow crystals of **5a,b** and **6a,b** were isolated in 80–95% yield (Scheme 1). The X-ray crystal structural analysis of **6a** revealed§ that a migration of the phenolato ligand to the γ-carbon atom of the allenylidene moiety had taken place (Fig. 1). As expected, the Rh–C(1) distance [2.037(4) Å] is significantly longer than in the allenylidene complex **1b** [1.855(5) Å][6] and nearly identical to the Rh–C bond lengths in the five-coordinate bis(alkynyl)hydridorhodium(III) compound [RhH(C≡CCPr$^i_2$OH)$_2$(PPr$^i_3$)$_2$] [2.032(4), 2.022(4) Å].[7] The Rh–C– C–C chain is almost linear with only a slight bending at C(1) and C(2). The two phenyl substituents at C(3) are orthogonal to each other, thus presumably minimizing the repulsion between the C–H units.

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

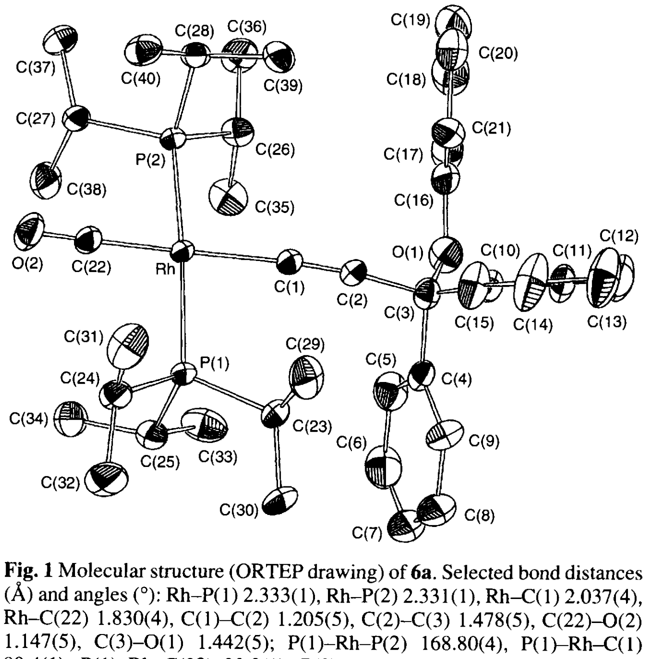


Fig. 1 Molecular structure (ORTEP drawing) of **6a**. Selected bond distances (Å) and angles (°): Rh–P(1) 2.333(1), Rh–P(2) 2.331(1), Rh–C(1) 2.037(4), Rh–C(22) 1.830(4), C(1)–C(2) 1.205(5), C(2)–C(3) 1.478(5), C(22)–O(2) 1.147(5), C(3)–O(1) 1.442(5); P(1)–Rh–P(2) 168.80(4), P(1)–Rh–C(1) 89.4(1), P(1)–Rh–C(22) 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(10) 113.7(4), C(2)–C(3)–O(1) 111.6(3).

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*-$[Rh(OMe)(CO)(PPr^i_3)_2]$ with CO leading to *trans*-$[Rh(CO_2Me)(CO)(PPr^i_3)_2]$,[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 allenylidenes thus generating alkoxy(vinyl)carbene ligands.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie and Degussa AG.

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.

‡ Selected ^{13}C 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, CO_2Me), 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], 167.2 (s, CO_2Me), 125.5 [dt, *J*(RhC) 42.6, *J*(PC) 20.3 Hz, Rh*C*≡C], 114.2 [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, Rh*C*≡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); $C_{40}H_{57}O_2P_2Rh$, $M = 734.74$; monoclinic, space group $P2_1/c$ (no.14), $Z = 4$, $a = 12.819(4)$, $b = 14.633(3)$, $c = 21.020(7)$, $\beta = 92.36(2)°$, $U = 3940(2)$ Å^3, $D_c = 1.239$ g cm^{-3}, $T = 293$ K, max $2\theta = 48°$, graphite-monochromated Mo-Kα radiation (λ = 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, −0.305 e 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.

References

1 J. P. Collmann, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, ch. 6; C. Elschenbroich and A. Salzer, *Organometallics*, VCH, Weinheim, 1992, ch. 14.
2 M. Schäfer, N. Mahr, J. Wolf and H. Werner, *Angew. Chem.*, 1993, **105**, 1377; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1315; R. Wiedemann, P. Steinert, J. Wolf and H. Werner, *J. Am. Chem. Soc.*, 1993, **115**, 9864; R. Wiedemann, J. Wolf and H. Werner, *Angew. Chem.*, 1995, **107**, 1359; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1244.
3 A. K. McMullen, J. P. Selegue and J.-G. Wang, *Organometallics*, 1991, **10**, 3421; H. E. Selnau and J. S. Merola, *J. Am. Chem. Soc.*, 1991, **113**, 4008; M. D. Fryzuk, L. Huang, N. T. McManus, P. Paglia, S. J. Rettig and G. S. White, *Organometallics*, 1992, **11**, 2979; G. Proulx and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 9802.
4 R. Wiedemann, P. Steinert, O. Gevert and H. Werner, *J. Am. Chem. Soc.*, 1996, **118**, 2495.
5 R. Wiedemann, Dissertation, Universität Würzburg, 1995.
6 H. Werner, T. Rappert, R. Wiedemann, J. Wolf and N. Mahr, *Organometallics*, 1994, **13**, 2721.
7 H. Werner, R. Wiedemann, N. Mahr, P. Steinert and J. Wolf, *Chem. Eur. J.*, 1996, **2**, 561.
8 T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 3411.
9 H. Le Bozec, K. Ouzzine and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 1989, 219; D. Pilette, K. Ouzzine, H. Le Bozec, P. H. Dixneuf, C. E. F. Rickard and W. R. Roper, *Organometallics*, 1992, **11**, 809.

Received, 12th March 1996; Com. 6/01751G