Allylrhodium Complexes $[\mathrm{Rh(\eta^3\text{-}2\text{-}RC_3H_4)(PPr^i{}_3)_2}]$ as Precursors for Carboxylato, Alkynyl(hydrido), Alkynyl(ethene) and Alkynyl(vinylidene) Rhodium Derivatives

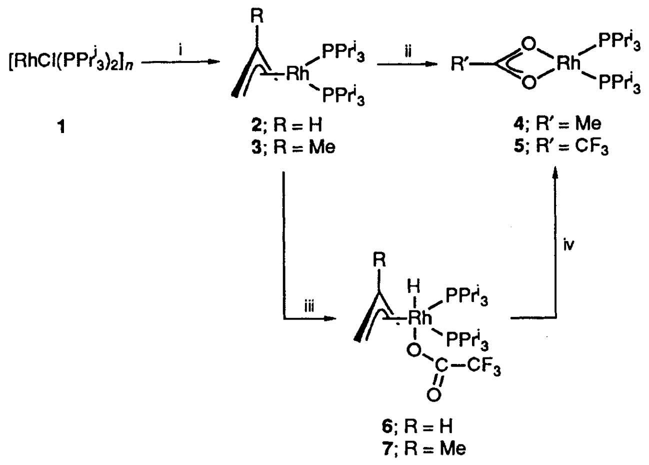
Martin Schäfer, Justin Wolf and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, W-8700 Würzburg, Germany

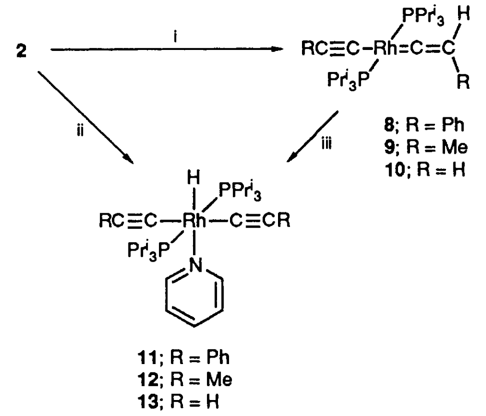
Allylrhodium complexes $[\mathrm{Rh(\eta^3\text{-}2\text{-}RC_3H_4(PPr^i{}_3)_2}]$ **2,3**, which are prepared from $[\mathrm{RhCl(PPr^i{}_3)_2}]_n$ **1** and allyl Grignard reagents, react with $\mathrm{R'CO_2H}$ ($\mathrm{R'}$ = Me, $\mathrm{CF_3}$) to give $[\mathrm{Rh(\eta^2\text{-}O_2CR')(PPr^i{}_3)_2}]$ **4,5** but with alk-1-ynes $\mathrm{RC{\equiv}CH}$ (R = $\mathrm{C_6H_5}$, Me, H) to give the alkynyl(vinylidene) compounds *trans*-$[\mathrm{Rh(C{\equiv}CR)({=}C{=}CHR)(PPr^i{}_3)_2}]$ **8–10**; in the presence of pyridine (py) the octahedral bis(alkynyl)hydrido derivatives $[\mathrm{RhH(C{\equiv}CR)_2(py)(PPr^i{}_3)_2}]$ **11–13** are obtained.

The high reactivity of $[\mathrm{RhCl(PPr^i{}_3)_2}]_n$ **1**,[1,2] which has been used as a starting material for the synthesis of square-planar and half-sandwich type vinylidene rhodium complexes,[3,4] has prompted us to find out whether other bis(triisopropylphosphine)rhodium(I) compounds of general composition $[\mathrm{RhX(PPr^i{}_3)_2}]$ are also accessible. In the present communication we describe the preparation of four representative examples with X = $\mathrm{C_3H_5}$, 2-$\mathrm{MeC_3H_4}$, $\mathrm{MeCO_2}$ and $\mathrm{CF_3CO_2}$ and illustrate their synthetic potential to form alkynyl(hydrido)-, alkynyl(ethene)- and in particular formerly unknown alkynyl(vinylidene)-rhodium derivatives.

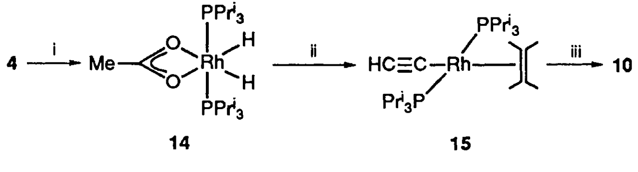
Compound **1**, generated *in situ* from $[\mathrm{RhCl(C_8H_{14})_2}]_2$ and $\mathrm{PPr^i{}_3}$,[1a] reacts with $\mathrm{C_3H_5MgBr}$ in diethyl ether and with 2-$\mathrm{MeC_3H_4MgCl}$ in tetrahydrofuran (THF)–diethyl ether to



Scheme 1 *Reagents, conditions and yields*: i, $(C_3H_5)MgBr$ in diethyl ether or $(2\text{-}MeC_3H_4)MgCl$ in THF–diethyl ether, 25 °C, 10 min, 70%; ii, $MeCO_2H$ in C_6H_6 or CF_3CO_2H in THF–diethyl ether, 25 °C, 1 h, 83% for **4** and 60% for **5**; iii, CF_3CO_2H in pentane–diethyl ether, −20 °C, 10 min, 90%; iv, C_6H_6, 40 °C, 10 min, 80%



Scheme 2 *Reagents, conditions and yields*: i, RC≡CH in pentane (for R = Me in pentane–NEt_3 1:1), 25 °C, 2 h (R = Ph), 6 h (R = Me), 10 h (R = H), 89% **8**, 49% **9**, 37% **10**; ii, RC≡CH and pyridine in pentane, 25 °C and 1 h for R = Ph, 40 °C and 1 h for R = Me, 25 °C and 3 h for R = H, 90% **11**, **12**, 70% **13**; iii, pyridine in pentane, 40 °C and 10 min for R = Ph, 40 °C and 20 min for R = Me, 25 °C and 3 h for R = H, 90%



Scheme 3 *Reagents, conditions and yields*: i, H_2, pentane, 25 °C, 10 min, 97%; ii, HC≡CH, pentane, −30 °C, 5 min, 52%; iii, HC≡CH, pentane, 25 °C, 2 h, 70%

give yellow air sensitive π-allyl complexes $[Rh(\eta^3\text{-}C_3H_5)L_2]$ **2**[5] and $[Rh(\eta^3\text{-}2\text{-}MeC_3H_4)L_2]$ **3** (Scheme 1).†‡ Further treatment of **2** and **3** with $MeCO_2H$ and CF_3CO_2H at room temperature affords the acetato and trifluoracetato derivatives $[Rh(\eta^2\text{-}O_2CR')L_2]$ **4**,**5** which are also obtained from **1** and $MeCO_2Na$ or CF_3CO_2K but in unsatisfactory yields. If the reactions of **2** and **3** with CF_3CO_2H are carried out at −20 °C, the octahedral rhodium(III) complexes $[RhH(\eta^3\text{-}2\text{-}RC_3H_4)(\eta^1\text{-}O_2CCF_3)L_2]$ **6**,**7**, formed by oxidative addition of the carboxylic acid to the coordinatively unsaturated metal centre, can be isolated. On warming to 30–40 °C, they lose propene or isobutene to give compound **5** almost quantitatively.

The allyl complex **2** does not only react with carboxylic acids $R'CO_2H$ but also with alk-1-ynes RC≡CH by elimination of propene (Scheme 2). For R = Ph, it has been shown that at least two equivalents of the alkyne are needed to convert **2** quantitatively into the alkynyl(vinylidene)metal complex *trans*-[Rh(C≡CPh)(=C=CHPh)L_2] **8**. Preliminary mechanistic studies indicate that on the way from **2** to **8** the alkyne(alkynyl) compound *trans*-[Rh(C≡CPh)(PhC≡CH)L_2] is intermediarily formed which rearranges possibly *via* [RhH(C≡CPh)$_2L_2$] to give **8**. For MeC≡CH, the presence of NEt_3 is essential for the formation of product **9** in good yield.

The new alkynyl(vinylidene) complexes **8–10** react smoothly and nearly quantitatively with an excess of pyridine by converting the vinylidene ligand into a metal-bound hydride and an alkynyl group (Scheme 2). The synthesis of the octahedral rhodium(III) derivatives **11–13** can also be achieved directly from **2**, RC≡CH and pyridine (py). In contrast to monoalkynyl(hydrido) compounds [RhH(C≡CR)Cl(py)(PPr$^i_3$)$_2$] (R = Ph, Me),[3] which if stirred in solution at room temperature lose pyridine to form *trans*-[RhCl(=C=CHR)(PPr$^i_3$)$_2$], the bis(alkynyl)hydrido complexes **11** and **12** are relatively inert and do not rearrange under the same conditions to give **8** and **9**.

The parent alkynyl(vinylidene)rhodium(I) compound **10**, which on treatment of **2** with acetylene, is obtained in only

---

† All new compounds gave satisfactory elemental analyses in accord with the assigned structures: **2** yellow, air-sensitive crystals, m.p. 118 °C (decomp.); **3** yellow, air-sensitive crystals, m.p. 69 °C (decomp.); **4** red, air-sensitive crystals, m.p. 110 °C (decomp.); **5** deep-red, moderately air-sensitive crystals, m.p. 136 °C (decomp.); **6** white crystals, m.p. 55 °C (decomp.); **7** white crystals, m.p. 60 °C (decomp.); **8** dark-green, slightly air-sensitive crystals, m.p. 100 °C (decomp.); **9** green, slightly air-sensitive crystals, m.p. 65 °C (decomp.); **10** green, air-sensitive crystals, m.p. 85 °C (decomp.); **11** white crystals, m.p. 65 °C (decomp.); **12** white crystals, m.p. 104 °C (decomp.); **13** white crystals, m.p. 90 °C (decomp.); **14** white crystals, m.p. 43 °C (decomp.); **15** orange, air-sensitive crystals, m.p. 80 °C (decomp.).

‡ *Selected spectroscopic data* (J and N values in Hz) for **3**: ^1H NMR (C_6D_6) δ 2.85 (s, H_{syn} of CH_2), 2.14 (m, PC*H*Me), 1.97 (d, J_{PH} 6.1, H_{anti} of CH_2), 1.82 (d, J_{RhH} 2.0, $C_3H_4CH_3$), 1.21 and 1.19 (both dd, J_{PH} 12.0, J_{HH} 7.1, PCHCH_3). For **7**: ^1H NMR (CD_2Cl_2, −60 °C) δ 3.63 (d, J_{PH} 8.3, H_{anti} of CH_2), 3.35 (s, br, H_{syn} of CH_2), 2.26 (m, PC*H*Me), 1.86 (d, J_{RhH} 2.0, $C_3H_4CH_3$), 1.19 and 1.09 (both dd, J_{PH} 12.7, J_{HH} 6.8, PCHCH_3), −27.05 (dt, $J_{PH} = J_{RhH}$ 13.9, RhH). For **8**: IR (KBr) ν/cm^{-1} 2070 (C≡C), 1611 (C=C); ^1H NMR (C_6D_6) δ 7.2 (m, C_6H_5), 2.72 (m, PC*H*Me), 1.55 (dt, J_{PH} 3.3, J_{RhH} 0.8, =C*H*Ph), 1.34 (dvirtualt, N 13.6, J_{HH} 7.0, PCHCH_3); ^{13}C NMR (C_6D_6) δ 311.29 (dt, J_{RhC} 49.8, J_{PC} 15.5, Rh=C), 136.98 (d, J_{RhC} 9.7, ≡*C*Ph), 115.80 (dt, J_{RhC} 12.9, J_{PC} 5.9, =*C*HPh), 25.69 (virtualt, N 21.2, P*C*HMe), 20.62 (s, PCH*C*H$_3$), signal of Rh–*C* obscured by signals of C_6H_5 carbons. For **10** IR (KBr) ν/cm^{-1} 1935 (C≡C), 1620 (C=C); ^1H NMR (C_6D_6) δ 3.22 (d, br, J_{RhH} 1.3, ≡CH), 2.89 (m, PC*H*Me), 1.37 (dvirtualt, N 13.4, J_{HH} 7.0, PCHCH_3), −0.13 (t, J_{PH} 3.4, =CH_2); ^{13}C NMR (C_6D_6) δ 308.98 (dt, J_{RhC} 48.0, J_{PC} 15.3, Rh=C), 121.70 (dt, J_{RhC} 36.6, J_{PC} 18.3, Rh–C), 118.77 (d, J_{RhC} 9.2, ≡CH), 92.42 (dt, J_{RhC} 14.1, J_{PC} 7.0, =CH_2), 25.13 (virtualt, N 20.9, P*C*HMe), 20.57 (s, PCH*C*H$_3$). For **13**: IR (KBr) ν/cm^{-1} 3290 (≡C–H), 2190 (Rh–H), 1940 (C≡C); ^1H NMR (C_6D_6) δ 10.03 (m, 2H of C_5H_5N), 6.75 (m, 3H of C_5H_5N), 3.05 (m, PC*H*Me), 2.25 (dt, J_{RhH} 1.7, J_{PH} 1.5, ≡CH), 1.25 (dvirtualt, N 13.0, J_{HH} 6.2, PCHCH_3), −18.10 (dt, J_{RhH} 16.0, J_{PH} 14.0, RhH). For **14**: ^1H NMR (C_6D_6) δ 2.02 (m, PC*H*Me), 1.95 (s, O_2CCH_3), 1.20 (dvirtualt, N 13.0, J_{HH} 6.5, PCHCH_3), −23.98 (dt, J_{RhH} 24.5, J_{PH} 15.0, RhH). For **15**: IR (hexane) ν/cm^{-1} 3280 (≡C–H), 1935 (C≡C); ^1H NMR (C_6D_6) δ 3.16 (dt, J_{RhH} 1.6, J_{PH} 3.4, C_2H_4), 2.93 (dt, J_{RhH} 1.8, J_{PH} 1.7, ≡CH), 2.47 (m, PC*H*Me), 1.32 (dvirtualt, N 12.1, J_{HH} 6.1, PCHCH_3); ^{13}C NMR (C_6D_6) δ 118.5 (dt, J_{RhC} 48.8, J_{PC} 20.5, Rh–C), 107.5 (dt, J_{RhC} 13.7, J_{PC} 2.0, ≡CH), 53.3 (d, J_{RhC} 10.7, C_2H_4), 23.47 (virtualt, N 18.6, P*C*HMe), 20.79 (s, PCH*C*H$_3$).

modest yield together with other, as yet unidentified, products, has also been prepared by a second route which is shown in Scheme 3. The formation of the ethylene compound **15** from **4** occurs *via* the dihydrido complex **14**, which reacts with HC≡CH at −30 °C by hydrogenation of the alkyne and abstraction of $MeCO_2H$. The reaction of **15** with acetylene at room temperature gives complex **10** in 70% yield. It should be mentioned that in contrast to **8** and **9**, the parent compound **10** reacts with one equivalent of pyridine to give an equilibrium mixture of **10** and **13** which only in the presence of an excess of pyridine can be transformed completely to the octahedral rhodium(III) derivative.

We finally note that bis(alkynyl)rhodium complexes containing a linear unit RC≡C–Rh–C≡CR have recently been prepared independently by Lewis[6] and Marder[7] using the four- and five-coordinate tetrakis(phosphine)rhodium(I) compounds $[Rh(PMe_3)_4]Cl$, $[RhMe(PMe_3)_4]$ and $[Rh(PBu^n{}_3)_4][BPh_4]$ as starting materials. Besides mononuclear complexes, oligomeric derivatives have also been isolated.[6,7] They may find application because of their nonlinear optical and liquid crystal properties.[8] Work is also in progress at our laboratory, employing both mono- and di-ynes,[9] following this strategy.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and DEGUSSA AG. We also thank Dr T. B. Marder for prompt information about his results.

Received, 19th June 1991; Com. 1/03023J

References

1 (*a*) Generation *in situ*: C. Busetto, A. D'Alfonso, F. Maspero, G. Perego and A. Zazetta, *J. Chem. Soc., Dalton Trans.*, 1977, 1828; (*b*) Isolation: H. Werner, J. Wolf and A. Höhn, *J. Organomet. Chem.*, 1985, **287**, 395; (*c*) Compound **1** is monomeric in benzene (ref. 2*a,b*) but dimeric in the solid state (ref. 2*c*).

2 (*a*) D. Schneider, Dissertation, Universität Würzburg, 1991; (*b*) D. Schneider and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 700; (c) J. Haas, Dissertation, Universität Kaiserslautern, 1990.

3 F. J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 406; H. Werner, F. J. Garcia Alonso, H. Otto and J. Wolf, *Z. Naturforsch., Teil B*, 1988, **43**, 722; H. Werner and U. Brekau, *Z. Naturforsch., Teil B*, 1989, **44**, 1438.

4 J. Wolf, H. Werner, O. Serhadli and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 414; H. Werner, J. Wolf, F. J. Garcia Alonso, M. L. Ziegler and O. Serhadli, *J. Organomet. Chem.*, 1987, **336**, 397.

5 The preparation of **2** from $[Rh(\eta^3\text{-}C_3H_5)(C_8H_{12})]$ and $PPr^i{}_3$ has already been reported: D. L. Thorn and J. A. Ibers, *Adv. Chem. Ser.*, 1982, **196**, 117.

6 S. J. Davies, B. F. G. Johnson, M. S. Khan and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1991, 187.

7 H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor and T. B. Marder, *J. Chem. Soc., Chem. Commun.*, 1991, 188.

8 T. B. Marder, G. Lesley, Z. Yuan, H. B. Fyfe, P. Chow, G. Stringer, I. R. Jobe, N. J. Taylor, I. D. Williams and S. K. Kurtz, in *Materials for Nonlinear Optics: Chemical Perspectives*, eds. G. D. Stucky, S. R. Marder and J. Sohn, *ACS Symp. Ser.* 455, American Chemical Society, Washington, DC, 1991, p. 605.

9 H. Werner, T. Rappert and J. Wolf, *Isr. J. Chem.*, 1990, **30**, 377; T. Rappert, Dissertation, Universität Würzburg, to be submitted.