

Stable Carbonyl- and Thiocarbonylrhodium(I) Complexes Containing σ -Bonded Phenyl and Vinyl Groups as Ligands

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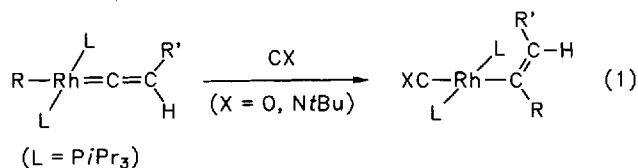
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The phenyl- and vinylrhodium(I) complexes *trans*-[Rh(R)(CO)(P*i*Pr₃)₂] (**2**, **3**) were prepared from the chloro derivative **1** and Grignard reagents. The corresponding thiocarbonyl compound *trans*-[Rh(CH=CH₂)(CS)(P*i*Pr₃)₂] (**7**) was obtained similarly from *trans*-[RhCl(CS)(P*i*Pr₃)₂] (**6**) and

CH₂=CHMgBr. The preparation of **6** occurred via *trans*-[RhCl(η²-S=C=S)(P*i*Pr₃)₂] (**5**) as intermediate. The carbonyl complexes **2** and **3** are quite inert in the presence of CO and do not react by migratory insertion to give acylrhodium derivatives.

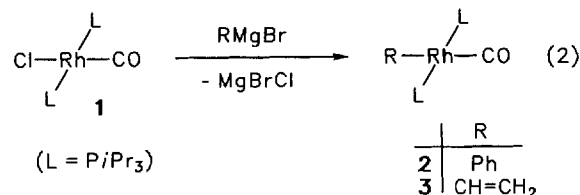
Recently, we reported that alkyl, aryl, and vinyl complexes of the general composition *trans*-[Rh(R)(=C=CHR')(P*i*Pr₃)₂] (R = CH₃, C₆H₅, CH=CH₂) react with CO or *tert*-butyl isocyanide by migratory insertion of the vinylidene ligand into the Rh–R bond to give substituted vinyl- and butadienylrhodium(I) derivatives [eq. (1)]^[1]. The C–C coupling occurs strictly stereoselectively independent of whether the substituent R' is a bulky alkyl (*t*Bu) or an aryl group.



Since vinylidenes and CO possess comparable bonding capabilities^[2], we considered it a challenging problem to prepare carbonylrhodium compounds *trans*-[Rh(R)(CO)(P*i*Pr₃)₂] and to find out whether on treatment with CO or CNR' these also react by migratory insertion to afford the corresponding acylmetal derivatives. There are numerous examples known of this type of C–C coupling^[3] which is one of the fundamental steps in several industrially important catalytic processes^[4].

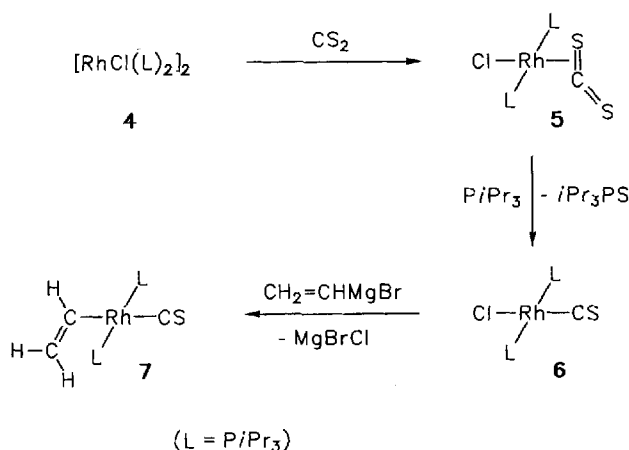
Under conditions similar to those used for the preparation of the vinylidene complexes *trans*-[Rh(R)(=C=CHR')(P*i*Pr₃)₂], the carbonylrhodium compound **1**^[5] reacts with phenyl and vinyl Grignard reagents to give the square-planar complexes **2** and **3** [see eq. (2)] in excellent yields. The yellow microcrystalline solids are only moderately air-sensitive and can be stored under argon for days without decomposition. The IR spectra of **2** and **3** display a strong CO stretching frequency at 1930 cm^{−1} located at exactly the same position as found for **1**. The chemical shifts of the signals of the phenyl and the vinyl protons as well as of the respective carbon atoms in the ¹H- and ¹³C-NMR spectra of **2** and **3** are almost identical with those of the complexes *trans*-[Rh(C₆H₅)(=C=CHR')(P*i*Pr₃)₂] and *trans*-[Rh(CH=CH₂)(=C=CHR')(P*i*Pr₃)₂] and thus confirmed the assumed similar donor/acceptor properties of CO and vinylidenes. It should be mentioned that the methylrhodium derivative *trans*-[Rh(CH₃)(CO)(P*i*Pr₃)₂], structur-

ally related to **2** and **3**, is also known but was prepared in our laboratory by a different route^[6].



Since not only CO and vinylidenes but also CS belongs to the series of strong π -acceptor ligands, the synthesis of thiocarbonylrhodium compounds of general composition *trans*-[Rh(R)(CS)(P*i*Pr₃)₂] was also attempted. The precursor complex *trans*-[RhCl(CS)(P*i*Pr₃)₂] (**6**) is obtained from the CS₂ compound **5** which is formed by treatment of the dimer **4**^[7] with CS₂ in benzene. The isolated yield of **5**, which is an orange remarkably stable solid, is 91%. The reaction of **5** with triisopropylphosphane in benzene proceeds smoothly and (after stirring at room temperature for 1 h) affords compound **6** quantitatively. In contrast to the IR spectrum of **5**, which shows two C=S stretching frequencies at 1235 and 1190 cm^{−1}, that of **6** displays only one band in that region (at 1280 cm^{−1}), the position of which is very similar to that of other thiocarbonylrhodium compounds such as *trans*-[RhCl(CS)(PPh₃)₂]^[8] and *trans*-[RhCl(CS)(PCy₃)₂]^[9]. In the ¹³C-NMR spectrum of **6**, the signal for the CS carbon atom appears at δ = 274.06 which due to Rh–C and P–C coupling is split into a doublet of triplets.

Compound **6** reacts slowly with an excess of CH₂=CHMgBr in benzene at 50 °C to give the vinyl(thiocarbonyl)rhodium(I) complex **7** in 62% yield. For the workup of the reaction mixture it is important to remove the non-reacted vinylmagnesium bromide with 1,2-dibromoethane because otherwise the isolation of the pure product is more difficult. While the position of the C=S stretching frequency in the IR spectrum of **7** is almost identical to that of **6**, the chemical shift of the signal of the thiocarbonyl carbon atom in the ¹³C-NMR spectra of **6** and **7** differs by ca. 27 ppm. The resonance of the metal-bonded vinyl α -carbon atom appears at about the same position as in the ¹³C-NMR spectra of **3** (δ = 173.68) and of *trans*-[Rh(CH=CH₂)(=C=CHPh)(P*i*Pr₃)₂] (173.57)^[11], which again



confirmed the analogous bonding capabilities of CO, CS, and vinylidenes^[2].

Despite these similarities in the ligand behavior, compounds **2** and **3** do not react with carbon monoxide under normal conditions (1 bar, 25 °C, C₆H₆). This is in sharp contrast to the reactivity of the vinylidene complexes *trans*-[Rh(R)(C=CHR')(PiPr₃)₂] (R = C₆H₅, CH=CH₂; R' = C₆H₅, *i*Bu) which on treatment with CO undergo migratory insertion to yield the corresponding carbonyl(vinyl) and carbonyl(butadienyl)rhodium derivatives^[1]. Since the vinyl compounds *trans*-[Rh(CH=CH₂)(C=CHR')(PiPr₃)₂] rearrange to η³-butadienyl complexes even in the absence of CO^[10], it seems that vinylidenes are superior to CO and CS for C–C coupling reactions. We note, however, that other carbonylrhodium(I) compounds such as *trans*-[Rh(C₆H₅)(CO)(PMe₃)₂] and *trans*-[Rh(C₂H₅)(CO)(PPh₃)₂], which are structurally related to **2** and **3**, smoothly undergo CO insertion by treatment with carbon monoxide to afford the corresponding acylmetal derivatives^[11].

In summary, we have shown that by starting from either *trans*-[RhCl(CO)(PiPr₃)₂] (**1**) or *trans*-[RhCl(CS)(PiPr₃)₂] (**6**) the corresponding square-planar aryl- and vinylrhodium complexes are accessible. At least the carbonyl compounds are kinetically quite stable which is unexpected insofar as the analogous vinylidenerhodium(I) complexes react both with and without CO by migration of the σ-bonded group R to the α-carbon of the vinylidene unit.

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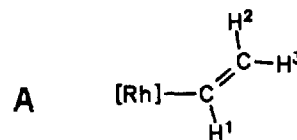
Experimental

All experiments were carried out under argon by means of the Schlenk-tube technique. The starting materials *trans*-[RhCl(CO)(PiPr₃)₂] (**1**)^[5] and [RhCl(PiPr₃)₂] (**4**)^[7] were prepared by published procedures. – Melting points: measured by DTA. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400, vt = virtual triplet.

1. trans-[Rh(C₆H₅)(CO)(PiPr₃)₂] (2): A solution of 160 mg (0.33 mmol) of **1** in 3 ml of benzene was treated at 10 °C with 1.0 ml of a 1.0 M solution (1.00 mmol) of PhMgBr in diethyl ether. Upon warming to 50 °C, the solution was stirred for 2 h, and then the solvent was removed in vacuo. The residue was extracted with 30 ml of pentane, the extract was filtered, and the filtrate was concentrated to ca. 3 ml in vacuo. Upon cooling to –78 °C for 2 d, a yellow microcrystalline solid precipitated which was separated from

the solution, washed three times with 2 ml of pentane (–20 °C) each and dried; yield 144 mg (87%), m.p. 54 °C (dec.). – IR (C₆H₆): $\tilde{\nu}$ = 1930 cm^{–1} [ν(C≡O)]. – ¹H NMR (200 MHz, C₆D₆): δ = 7.44 (m, 2H, *o*-C₆H₅), 7.15 (m, 3H, *m*- and *p*-C₆H₅), 2.57 (m, 6H, PCHCH₃), 1.27 [dvt, *N* = 13.8, *J*(HH) = 7.1 Hz, 36H, PCHCH₃]. – ¹³C NMR (100.6 MHz, C₆D₆): δ = 197.04 [dt, *J*(RhC) = 54.4, *J*(PC) = 14.4 Hz, CO], 172.22 [dt, *J*(RhC) = 27.9, *J*(PC) = 14.4 Hz, *ipso*-C₆H₅], 140.14 [t, *J*(PC) = 2.6 Hz, C₆H₅], 128.83 [dt, *J*(RhC) = 1.4, *J*(PC) = 1.4 Hz, C₆H₅], 121.88 [t, *J*(PC) = 1.1 Hz, C₆H₅], 26.08 [dvt, *N* = 19.9, *J*(RhC) = 1.4 Hz, PCHCH₃], 20.26 (s, br, PCHCH₃). – ³¹P NMR (81.0 MHz, C₆D₆): δ = 46.97 [d, *J*(RhP) = 143.7 Hz]. – C₂₃H₄₇OP₂Rh (504.5): calcd. C 54.76, H 9.39; found C 55.21, H 9.20.

2. trans-[Rh(CH=CH₂)(CO)(PiPr₃)₂] (3): A solution of 170 mg (0.35 mmol) of **1** in 3 ml of benzene was treated at room temp. with 0.7 ml of a 1.0 M solution (0.70 mmol) of CH₂=CHMgBr in THF. After stirring of the reaction mixture for 2 h at 40 °C, it was worked up analogously as described for **2**. Pale yellow solid; yield 119 mg (74%), m.p. 135 °C (dec.). – IR (C₆H₆): $\tilde{\nu}$ = 1930 cm^{–1} [ν(C≡O)]. – ¹H NMR (400 MHz, C₆D₆, see A): δ = 7.61 [dddt, *J*(RhH¹) = 1.2, *J*(PH¹) = 3.5, *J*(H¹H²) = 20.1, *J*(H¹H³) = 14.2 Hz, 1H, H¹], 6.30 [m, in ¹H{³¹P} ddd, *J*(RhH³) = 2.8, *J*(H¹H³) = 14.2, *J*(H²H³) = 4.5 Hz, 1H, H³], 5.51 [m; in ¹H{³¹P} ddd, *J*(RhH²) = 0.8, *J*(H¹H²) = 20.1, *J*(H²H³) = 4.5 Hz, 1H, H²], 2.37 (m, 6H, PCHCH₃), 1.26 [dvt, *N* = 13.5, *J*(HH) = 7.0 Hz, 36H, PCHCH₃]. – ¹³C NMR (100.6 MHz, C₆D₆): δ = 197.77 [dt, *J*(RhC) = 55.1, *J*(PC) = 13.8 Hz, CO], 173.68 [dt, *J*(RhC) = 27.1, *J*(PC) = 16.6 Hz, Rh–CH=CH₂], 123.19 [t, *J*(PC) = 4.3 Hz, Rh–CH=CH₂], 20.64 [dvt, *N* = 20.5, *J*(RhC) = 1.4 Hz, PCHCH₃], 20.32 (s, PCHCH₃). – ³¹P NMR (162.0 MHz, C₆D₆): δ = 50.80 [d, *J*(RhP) = 143.5 Hz]. – C₂₁H₄₅OP₂Rh (478.4): calcd. C 52.72, H 9.48; found C 52.98, H 9.74.



3. trans-[RhCl(η²-S=C=S)(PiPr₃)₂] (5): A solution of 200 mg (0.22 mmol) of **4** in 4 ml of benzene was treated at room temp. with 27 μl (34 mg, 0.44 mmol) of CS₂ which led to a change of color from red to orange. After stirring of the reaction mixture for 10 min, the solvent was removed, the residue was dissolved in 4 ml of hexane, and the solution was chromatographed on Al₂O₃ (neutral, activity grade V, height of column 5 cm). With hexane, an orange fraction was eluted which was evaporated to dryness in vacuo. The orange solid was washed three times with 1 ml of pentane (–20 °C) each and dried; yield 212 mg (91%), m.p. 140 °C. – IR (C₆H₆): $\tilde{\nu}$ = 1235, 1190 cm^{–1} [ν(C=S)]. – ¹H NMR (200 MHz, CDCl₃): δ = 2.66 (m, 6H, PCHCH₃), 1.39 [dvt, *N* = 13.9, *J*(HH) = 7.1 Hz, 18H, PCHCH₃], 1.28 [dvt, *N* = 13.3, *J*(HH) = 7.1 Hz, 18H, PCHCH₃]. – ¹³C NMR (50.3 MHz, CDCl₃): δ = 233.91 [dt, *J*(RhC) = 23.5, *J*(PC) = 4.4 Hz, C(S)=S], 22.60 (vt, *N* = 19.1 Hz, PCHCH₃), 20.24, 19.67 (both s, PCHCH₃). – ³¹P NMR (81.0 MHz, CDCl₃): δ = 28.44 [d, *J*(RhP) = 106.1 Hz]. – C₁₉H₄₂ClP₂RhS₂ (535.0): calcd. C 42.66, H 7.91, S 11.99; found C 42.21, H 7.72, S 11.58.

4. trans-[RhCl(CS)(PiPr₃)₂] (6): A solution of 205 mg (0.38 mmol) of **5** in 4 ml of benzene was treated with 97 μl (80 mg, 0.50 mmol) of PiPr₃ and stirred for 1 h at room temp. The solvent was removed, the residue was dissolved in 4 ml of hexane, and the solution was chromatographed on Al₂O₃ (acidic, activity grade I, height

of column 5 cm). With benzene, an orange fraction was eluted which was worked up as described for **5**. Orange microcrystalline solid; yield 181 mg (94%), m.p. 185 °C. – IR (C_6H_6): $\tilde{\nu} = 1280 \text{ cm}^{-1}$ [$\nu(\text{C}\equiv\text{S})$]. – ^1H NMR (200 MHz, CDCl_3): $\delta = 2.77$ (m, 6H, PCHCH_3), 1.28 [dvt, $N = 13.9$, $J(\text{HH}) = 7.1 \text{ Hz}$, 36H, PCHCH_3]. – ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 274.06$ [dt, $J(\text{RhC}) = 70.0$, $J(\text{PC}) = 12.7 \text{ Hz}$, CS], 23.35 [dvt, $N = 21.0$, $J(\text{RhC}) = 1.3 \text{ Hz}$, PCHCH_3], 20.00 (s, PCHCH_3). – ^{31}P NMR (162.0 MHz, CDCl_3): $\delta = 46.31$ [d, $J(\text{RhP}) = 148.4 \text{ Hz}$]. – $\text{C}_{19}\text{H}_{42}\text{ClP}_2\text{RhS}$ (502.9): calcd. C 45.38, H 8.42, S 6.37; found C 45.40, H 7.99, S 6.52.

5. trans-[Rh(CH=CH₂)(CS)(PiPr₃)₂] (7): A solution of 140 mg (0.28 mmol) of **6** in 2 ml of benzene was treated with 1.0 ml of a 1.0 M solution (1.00 mmol) of $\text{CH}_2=\text{CHMgBr}$ in THF and then stirred for 2 h at 50 °C. A change of color from orange to red occurred. After removal of the solvent, the oily residue was layered with 10 ml of pentane/1,2- $\text{C}_2\text{H}_4\text{Br}_2$ (30:1). The mixture was stirred for 10 min, and then 20 ml of pentane was added. A colorless precipitate formed which was filtered off. The filtrate was evaporated to dryness in vacuo, and the residue was dissolved in 4 ml of pentane. During storage of the solution for 2 d at –78 °C, red crystals precipitated which were separated, washed three times with 1 ml of pentane (–20 °C) each and dried; yield 85 mg (62%), m.p. 126 °C (dec.). – IR (C_6H_6): $\tilde{\nu} = 1270, 1250 \text{ cm}^{-1}$ [$\nu(\text{C}\equiv\text{S})$]. – ^1H NMR (400 MHz, C_6D_6): $\delta = 7.29$ [dddt, $J(\text{RhH}^1) = 1.0$, $J(\text{PH}^1) = 3.2$, $J(\text{H}^1\text{H}^2) = 20.2$, $J(\text{H}^1\text{H}^3) = 14.6 \text{ Hz}$, 1H, H^1], 6.13 [dddt, $J(\text{RhH}^3) = 2.2$, $J(\text{PH}^3) = 2.0$, $J(\text{H}^1\text{H}^3) = 14.6$, $J(\text{H}^2\text{H}^3) = 4.6 \text{ Hz}$, 1H, H^3], 5.29 [dddt, $J(\text{RhH}^2) = 1.3$, $J(\text{PH}^2) = 2.2$, $J(\text{H}^1\text{H}^2) = 20.2$, $J(\text{H}^2\text{H}^3) = 4.6 \text{ Hz}$, 1H, H^2], 2.64 (m, 6H, PCHCH_3), 1.33 [dvt, $N = 13.6$, $J(\text{HH}) = 7.1 \text{ Hz}$, 36H, PCHCH_3]; for the assignment of protons H^1 , H^2 , and H^3 see A. – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 300.80$ [dt, $J(\text{RhC}) = 56.0$, $J(\text{PC}) = 13.2 \text{ Hz}$, CS], 172.90 [dt, $J(\text{RhC}) = 23.3$, $J(\text{PC}) = 17.2 \text{ Hz}$, Rh–CH=CH₂], 124.33 [t, $J(\text{PC}) = 4.1 \text{ Hz}$, Rh–CH=CH₂], 25.19 (vt, $N = 20.3 \text{ Hz}$, PCHCH_3), 20.33 (s, PCHCH_3). – ^{31}P NMR (162.0 MHz, C_6D_6):

$\delta = 46.31$ [d, $J(\text{RhP}) = 148.4 \text{ Hz}$]. – MS (70 eV), m/z (%): 494 (26) [M^+], 467 (9) [$\text{M}^+ - \text{C}_2\text{H}_3$], 334 (66) [$\text{M}^+ - \text{PiPr}_3$]. – $\text{C}_{21}\text{H}_{45}\text{P}_2\text{RhS}$ (494.5): calcd. C 51.01, H 9.17, S 6.48; found C 50.92, H 8.86, S 6.45.

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