Preparation and Reactions of Bis(isocyanide)(η^5-indenyl)rhodium(I) Complexes†

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The bis(aryl isocyanide)(η^5-indenyl)rhodium(I) complexes [Rh(η-C_9H_7)(RNC)$_2$] [**1**; R = 4-Br-2,6-$Me_2C_6H_2$, 2,6-$Me_2C_6H_3$, or 2,4,6-Bu$^t_3C_6H_2$] were prepared by the reactions of [Rh(RNC)$_3$Cl] or a mixture of [{RhCl(cod)}$_2$] (cod = cyclo-octa-1,5-diene) and RNC with indenyl-lithium. Reaction of (**1**) with tetracyanoethylene (tcne) or methyl iodide gave an olefin complex, [Rh(η^5-C_9H_7)(RNC)(tcne)], or an iminoacyl complex, [Rh(η^5-C_9H_7)(RNC){C(Me)=NR}I], respectively.

It has been reported that bis(isocyanide) complexes of η^5-pentamethylcyclopentadienyl- or η^5-indenyl-rhodium(I) play a role as a precursor in the activation of carbon–hydrogen bonds.[1] Methods of preparation of the complexes are (i) by the reaction of [Rh(η^5-C_9H_7)(C_2H_4)$_2$] with isocyanide[2] and (ii) by the reduction of [Rh(η^5-C_5Me_5)(RNC)X_2] (R = Bu^{t}CH$_2$) with sodium amalgam or with sodium dihydronaphthylide in the presence of isocyanide.[1] We report here a convenient synthesis of bis(isocyanide)(η^5-indenyl)rhodium(I) complexes by the reaction of indenyl-lithium with [Rh(RNC)$_3$Cl] (R = aryl)[3] or a mixture of [{RhCl(cod)}$_2$] (cod = cyclo-octa-1,5-diene) and isocyanide.

Results and Discussion

Addition of indenyl-lithium to the appropriate chlorotris(isocyanide)rhodium(I) complex in a mixture of benzene and diethyl ether produced brownish yellow complex (**1**), formulated as [Rh(η-C_9H_7)(RNC)$_2$] [R = 4-Br-2,6-$Me_2C_6H_2$ (**1a**), 2,6-$Me_2C_6H_3$ (**1b**), or 2,4,6-Bu$^t_3C_6H_2$ (**1c**)]. The i.r. spectrum showed two peaks near 2 100 cm^{-1}, assignable to terminal isocyanide groups. The ^{1}H n.m.r. spectrum in $CDCl_3$ showed a characteristic pattern of the indenyl group at δ 5.60 [d, *J*(HH) = 2.0] and 6.30 [q, *J*(HH) = *J*(RhH) = 2.0 Hz] which have been observed often in η^5-indenyl complexes.[4]

The complexes were also obtained by treatment of a mixture of [{RhCl(cod)}$_2$] and RNC with indenyl-lithium.

Treatment of (**1a**) with tetracyanoethylene (tcne) produced the olefin complex [Rh(η^5-C_9H_7)(4-Br-2,6-$Me_2C_6H_2$NC)(tcne)] (**2a**) in 90% yield. The i.r. spectrum showed two peaks at 2 219 and 2 157 cm^{-1}, assignable to ν(C≡N) and ν(N≡C) (cyanide and isocyanide) stretching bands respectively. Similar complexes, [Rh(η^5-C_9H_7)(RNC)(tcne)] [R = 2,6-$Me_2C_6H_2$ (**2b**) or 2,4,6-Bu$^t_3C_6H_2$ (**2c**)] were prepared from complexes (**1b**) and (**1c**) respectively.

When methyl iodide was added to a solution of (**1a**) in benzene, an immediate reaction occurred to give the iminoacyl complex [Rh(η^5-C_9H_7)(RNC){C(Me)=NR}I] (**3a**; R = 4-Br-2,6-$Me_2C_6H_2$). The i.r. spectrum showed the presence of the terminal isocyanide and iminoacyl groups at 2 147 and 1 661 cm^{-1} respectively.[5]

A similar type of complex, [Rh(η^5-C_5Me_5){C(C_6H_4Me-4)=NCH$_2$Bu^t}(PMe$_3$)], has been obtained from the reaction of [Rh(η^5-C_5Me_5)(CNCH$_2$Bu^t)Br$_2$] with 4-MeC_6H_4MgBr, followed by addition of trimethylphosphine.[1]

Experimental

The preparations were carried out under an atmosphere (*ca.* 10^5 Pa) of nitrogen. Infrared and ^{1}H n.m.r. spectra were measured on Shimazu IR-27G and JEOL C-60HL spectrometers respectively. The isocyanides[3b,6] and [Rh(RNC)$_3$Cl][3] were prepared by procedures described in the literature.

Preparation of [Rh(η^5-C_9H_7)(RNC)$_2$] (**1**) *and* [Rh(η^5-C_9H_7)(RNC)(tcne)] (**2**).—Representative examples are described.

Preparation of (**1a**). To a suspension of [Rh(4-Br-2,6-$Me_2C_6H_2$NC)$_3$Cl] (0.325 g, 0.42 mmol) in benzene–diethyl ether (3:2, 25 cm^3) was added LiC_9H_7 (0.16 mmol) in ether (3 cm^3). After stirring for 2 h at room temperature, aqueous NH$_4$Cl was added. The organic layer was decanted and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The organic layer was dried over Na$_2$SO$_4$ and chromatographed on alumina (column height, 10 cm) (containing 10% H$_2$O). Elution with CH$_2$Cl$_2$ gave an orange solution. Removal of the solvent and crystallization of the residue from CH$_2$Cl$_2$–hexane at 0 °C gave dark orange crystals of (**1a**), yield 0.16 g (59%), m.p. 160 °C (decomp.) (Found: C, 50.8; H, 3.65; N, 4.35. Calc. for $C_{27}H_{23}Br_2N_2Rh$: C, 50.8; H, 3.65; N, 4.40%). I.r. (Nujol): 2 106 and 2 038 cm^{-1}. N.m.r. ($CDCl_3$): δ 2.44 (s, 2,6-Me$_2$), 5.59 [d, *J*(HH) = 2.0], 6.30 [q, *J*(HH) = 2.0, *J*(Rh–H) = 2.0 Hz], *ca.* 7.0 (aromatic protons). Electronic spectrum (CH$_2$Cl$_2$): $\lambda_{max.}$ 391 (ε 11 950) and 315 nm (16 360 dm^3 mol^{-1} cm^{-1}).

The following complexes were prepared by similar procedures. [Rh(η^5-C_9H_7)(2,6-$Me_2C_6H_3$NC)$_2$] (**1b**), yield 62%, m.p. 143—146 °C (decomp.) (Found: C, 67.65; H, 5.25; N, 5.80. Calc. for $C_{27}H_{25}N_2Rh$: C, 67.5; H, 5.25; N, 5.85%). I.r. (Nujol): 2 110 and 2 045 cm^{-1}. Electronic spectrum (CH$_2$Cl$_2$): $\lambda_{max.}$ 390 (ε 18 260) and 315 nm (27 390 dm^3 mol^{-1} cm^{-1}). [Rh(η^5-C_9H_7)(2,4,6-Bu$^t_3C_6H_2$NC)$_2$] (**1c**), yield 60%, m.p. 164—167 °C (decomp.) (Found: C, 75.0; H, 9.05; N, 5.50. Calc. for $C_{47}H_{65}N_2Rh$: C, 74.2; H, 8.60; N, 3.70%). I.r. (Nujol): 2 054 and 2 107 cm^{-1}. N.m.r. ($CDCl_3$): δ 1.34 (s, 4-Bu^t), 1.50 (s, 2,6-Bu^t), 5.28 [d, *J*(HH) = 2.0], 6.39 [q, *J*(HH) = *J*(Rh–H) = 2.0 Hz], and *ca.* 7.0 (aromatic protons). Electronic spectrum (CH$_2$Cl$_2$): $\lambda_{max.}$ 397 (ε 6 520) and 268 nm (21 180 dm^3 mol^{-1} cm^{-1}).

Preparation of [Rh(η^5-C_9H_7)(2,4,6-Bu$^t_3C_6H_2$NC)(tcne)] (**2c**). A mixture of (**1c**) (0.05 g, 0.66 mmol) and tcne (0.01 g, 0.078 mmol) in CH$_2$Cl$_2$ (10 cm^3) was stirred for 0.5 h at room temperature. Solvent was removed *in vacuo* and the residue was chromatographed on alumina (containing 10% H$_2$O). Elution with benzene–CH$_2$Cl$_2$ (2:1) gave a yellow solution. Crystallization from benzene–hexane gave orange crystals of (**2c**), yield 93%, m.p. 190 °C (decomp.) (Found: C, 66.5; H, 5.95; N, 11.2.

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Calc. for $C_{34}H_{36}N_5Rh$: C, 66.1; H, 5.90; N, 11.3%). I.r. (Nujol): 2 214 and 2 149 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 441 (ε 3 670), 358 (3 120), and 268 nm (25 100 dm^3 mol^{-1} cm^{-1}). [Rh(η^5-C_9H_7)(4-Br-2,6-$Me_2C_6H_2NC$)(tcne)] (**2a**), yield 90%, m.p. 220 °C (decomp.) (Found C, 52.0; H, 2.75; N, 12.45. Calc. for $C_{24}H_{15}BrN_5Rh$: C, 51.8; H, 2.70; N, 12.6%). I.r. (Nujol): 2 219 and 2 157 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 438 (ε 3 770), 367 (3 110), 288 (21 000), and 264 nm (21 700 dm^3 mol^{-1} cm^{-1}). [Rh(η^5-C_9H_7)(2,6-$Me_2C_6H_3NC$)(tcne)] (**2b**), yield 75%, m.p. 206—209 °C (decomp.) (Found: C, 61.4; H, 13.5; N, 15.2. Calc. for $C_{24}H_{16}N_5Rh$: C, 60.4; H, 13.4; N, 14.65%). I.r. (Nujol): 2 217 and 2 160 cm^{-1}. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 451 (ε 5 450), 366 (3 360), and 213 nm (20 300 dm^3 mol^{-1} cm^{-1}).

Preparation of [Rh(η^5-C_9H_7)(4-Br-2,6-$Me_2C_6H_2NC$)-{C(Me)=NR}I]·CH_2Cl_2 (**3a**).—A solution of (**1a**) (0.1 g, 0.16 mmol) and MeI (0.1 cm^3) in benzene (10 cm^3) was stirred at room temperature. The mixture was chromatographed on alumina (containing 10% H_2O). Elution with benzene gave an orange solution. Orange crystals of (**3a**), yield 0.074 g (53%), m.p. 186—189 °C (decomp.) were obtained by recrystallization from CH_2Cl_2 (Found: C, 40.5; H, 3.25; N, 3.20. Calc. for $C_{29}H_{28}Br_2Cl_2IN_2Rh$: C, 40.25; H, 3.25; N, 3.25%). I.r. (Nujol): 2 147 and 1 661 cm^{-1}. N.m.r. ($CDCl_3$): δ 1.20 (s, C–CH_3), 2.53 (s, CH_3 of RNC), 3.18 (s, CH_3 of =NR), 5.60 [*J*(HH) = 2.0], and 6.33 [q, *J*(HH) = 2.0, *J*(Rh–H) = 2.0 Hz].

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