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Rhodium(I) Complexes with Benzothiazole

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Metal complexes with the ligand benzothiazole (BT) and substituted benzothiazoles have been extensively investigated [1–5], but no examples of (Rh(I)–BT complexes can be found in the literature. Recently the oxidative addition of 2-chloro derivatives of 5-methyl-1,3-thiazole and benzothiazole to d^8 and d^{10} metal complexes has been reported [6] but iridium(I) and not rhodium(I) was investigated.

As an extension of previous studies on the reactivity of the coordinated benzothiazole [7], we have investigated the reaction of BT with [Rh(1,5-cyclooctadiene)Cl]$_2$ (I) and [Rh(C$_2$H$_4$)$_2$Cl]$_2$.

From the reaction of (I) with an excess of BT in boiling toluene under nitrogen a yellow compound analyzing as RhCl(BT)(COD) can be isolated*. Its i.r. spectrum** shows, in addition to the bands of the coordinated COD, bands at 1462 (νC=N), 1412 (νS–C=N), 697 (νC–S) cm^{-1} due to the coordinated BT. These bands are at 1473, 1425 and 667 cm^{-1} respectively in the free ligand (film). The shift of the νC–S towards higher energy implies an increased dπ–pπ contribution between sulphur and the ring π-system [8]. The lowering of νC=N suggests that the C=N bond is loosened upon coordination. The far i.r. spectrum of the compound shows two bands at 278 and 260 cm^{-1} due to νRh–Cl as demonstrated by exchange with NaI. They are attributable to a bridging Cl more than to terminal clorine [9, 10]. These features suggest a dimeric structure [Rh(COD)(BT)Cl]$_2$ (II), with Rh(I) pentacoordinated in the solid state.

The ligand BT, as a rule, coordinates to the metal through the N-atom [1–4, 7] or through the S-atom [5], via a σ-donation. Nevertheless, an interaction of the metal with the conjugated $S\overset{\cdots}{-}C\overset{\cdots}{-}N$ system via a π-bond cannot be ruled out. In the latter case one would expect that the H^2 atom of the coordinated benzothiazole ring would be much more acidic than in the free ligand.

The ^{1}H n.m.r. spectrum of compound (II) in CDCl$_3$ shows resonances at 0.9 (s, 1H, H^2), 1.25 (d, 1H, H^4, J_{7-6} = 8.0 Hz), 2.14 (d, 1H, H^7, J_{4-5} = 7.5 Hz), 2.5 τ (m, 2H, H^{5,6})*. These resonances are at 1.10, 1.94, 2.16 and 2.64 τ respectively in the spectrum of the free ligand in CDCl$_3$. The signals of the coordinated COD in (II) are found at 5.82 (4H), 7.50 (4H) and 8.20 τ (4H) and they are all shifted upfield with respect to (I) (about 0.03 τ).

Such a dramatic change in the ^{1}H n.m.r. spectrum of the coordinated benzothiazole is not encountered in other metal complexes in which BT is bonded through the N atom [7] neither can be interpreted assuming a σ-coordination of the benzothiazole through the S atom. Comparison of the ^{1}H n.m.r. spectrum of (II) with those of Ag(BT)NO$_3$ and Ag(BT)$_2$NO$_3$ reveals that the H^2 is more acidic in (II) ($\Delta\tau$ = 0.2 with respect to 0.09 in Ag(BT)NO$_3$ and 0.03 in Ag(BT)$_2$NO$_3$). Moreover, in the silver complexes the phenyl proton resonances are unchanged with respect to the free ligand. The ^{1}H n.m.r. features of complex (II) seem to support a coordination of benzothiazole through a π-bond either localized on the S–C–N moiety or extended to the whole molecule of the BT. This could explain the changes in the pattern of the phenyl protons. The u.v. and visible spectrum in benzene is typical of tetracoordinate Rh(I)**.

Heating of (II) *in vacuo* at 140 °C causes loss of BT and (II) is regenerated. If (II) is heated in the presence of free BT the complex is recovered unalterated.

When [Rh(C$_2$H$_4$)$_2$Cl]$_2$ is allowed to react with an excess of BT, two mol of ethylene per Rh atom are evolved and the complex [Rh(BT)$_2$Cl]$_2$ (III) is isolated***. Its i.r. spectrum in Nujol shows bands of the coordinated benzothiazole at 1450 (νC=N), 1415 (νS–C=N), 705 (νC–S), 295 and 260 cm^{-1} (νRh–Cl bridging). Unfortunately, its low solubility in common non-coordinating solvents prevents the ^{1}H n.m.r. spectrum to be recorded. Conversely, in DMSO-d$_6$ the ligands are displaced and the signals due to the free ligand are observed in the spectrum even in the presence of an excess of free BT.

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*Analyses. Required for C$_{15}$H$_{17}$ClNRhS: C, 47.2; H, 4.50; Cl, 9.29; N, 3.67; S, 8.38%. Found: C, 47.15; H, 4.38; Cl, 9.25; N, 3.68; S, 8.29. M.p.: dec. from 140 °C. Diamagnetic. U.v. and visible maxima (1.01 × 10^{-3} *M* in benzene): 280 (ϵ = 7250), 385 nm (ϵ = 1150).

**Solid sample in Nujol mull.

*τ values are given with respect to TMS as internal standard.

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***Analyses. C$_{14}$H$_{10}$ClN$_2$RhS$_2$ requires: C, 41.15; H, 2.47; Cl, 8.68; N, 6.85; S, 15.66%. Found: C, 40.97; H, 2.40; Cl, 8.65; N, 6.80; S, 14.99. M.p.: dec. above 260 °C. Diamagnetic.

Both complexes (II) and (III) show some interesting catalytic properties. (III) promotes the dimerization of acetone to diacetone alcohol and mesityl oxide and the dimerization of benzaldehyde.

It must be emphasized that the Rh–BT complexes potentially present two catalytic sites: the metal atom and the C^2 of the ligand BT. It is known that the ylide form of alkylammonium salts of benzothiazole is able to catalyze aldehyde dimerization [11]. In our case the coordination of benzothiazole to the metal could enhance the H^2 acidity and permit the formation of the carbanion acting as the catalytic species*.

Complex (II) is found to hydrogenate acetone to isopropyl alcohol, but still it is not clear which is the effective catalytic species.

Studies are in progress in order to investigate the role played by the two catalytic sites in different processes.

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*The products of dimerization of acetone were determined by v.p.c. using a Carbowax 400 2 m column, temperature of the column 110 °C, gas carrier N_2 40 cm^3 min^{-1}.

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