Preliminary communication

Novel homonuclear disproportionation of $[Rh(CO)_3P-i-Pr_3]_2$ induced by nitrogen bases; evidence for the existence of the homonuclear ion pair, $[Rh(CO)(P-i-Pr_3)_2(amine)]^+[Rh(CO)_4]^-$

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Abstract

The single Rh–Rh bond, in the dimeric rhodium(0) complex $[Rh(CO)_3P-i-Pr_3]_2$, has been found to undergo facile homonuclear disproportionation which in the presence of a nitrogen base, e.g. triazole, imidazole or 4-aminopyridine, gives the homonuclear ion pair, $[Rh(CO)(P-i-Pr_3)_2(B)]^+[Rh(CO)_4]^-$.

The homonuclear disproportionation reaction of metal-metal bonded dinuclear carbonyl metals has been of interest to the organometallic chemist [1], and most of the studies have been limited to the reactions of $Co_2(CO)_8$ with a variety of Lewis bases [2]. However, no studies have appeared on the rhodium analogue, $Rh_2(CO)_8$, because of its instability under normal conditions [3]. Recently, we isolated the fairly stable dimer complexes, $[Rh(CO)_3PR_3]_2$ ($PR_3 = P-i-Pr_3$ (1); $P-n-Bu-t-Bu_2$, $P(cyclo-C_5H_9)_3$), from the reaction mixture of syngas converting to ethylene glycol with rhodium/ PR_3 / amine as catalyst [4]. A full crystallographic study of 1 has revealed the existence of a single unbridged rhodium(0)-rhodium(0) bond [5]. Here we report spectroscopic evidence for the homonuclear ion pair, $[Rh(CO)(P-i-Pr_3)_2(B)]^+[Rh(CO)_4]^-$ (2) (B = nitrogen base), which is a product of nitrogen base induced disproportionation of 1 in THF and 1,3-dimethyl-2-imidazolidinone (DMI) (eq. 1).

$$\begin{bmatrix} \operatorname{Rh}(\operatorname{CO})_{3}\operatorname{PR}_{3} \end{bmatrix}_{2} + \operatorname{B} \stackrel{^{\wedge}}{\rightleftharpoons} \begin{bmatrix} \operatorname{Rh}(\operatorname{CO})(\operatorname{PR}_{3})_{2}(\operatorname{B}) \end{bmatrix}^{+} \begin{bmatrix} \operatorname{Rh}(\operatorname{CO})_{4} \end{bmatrix}^{-} + \operatorname{CO}$$
(1)
(1) (2)

(B = nitrogen base)

When an excess of 1-methylimidazole (Im-1-Me) was added to a THF solution of 1 at $20 \degree C$ under 1 atm of CO, a marked increase in the specific conductivity of the solution was observed, indicating the generation of some charged species. Concom-

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itant and stoichiometric evolution of carbon monoxide, in agreement with eq. 1, was observed.

Figure 1 shows the IR and ${}^{31}P{}^{1}H$ NMR spectra of these solutions. Upon addition of Im-1-Me an infrared band at 1950 cm⁻¹ assigned to the dimer **1** disappeared, while new bands at 1895(vs) and 1980(m) cm⁻¹ progressively developed. In the presence of an excess of Im-1-Me, the ${}^{31}P{}^{1}H$ NMR spectrum of the THF solution of **1** consists of an AA'XX' multiplet at δ 70.6 ppm, due to **1**, and a new doublet at δ 45.6 with J(Rh-P) 116.8 Hz. Other species, such as the free phosphine, were not detected. In agreement with the IR spectra, the doublet signal increased at the expense of the multiplet signal.

In the presence of 35 equimolar amounts of Im-1-Me, the ¹³C NMR spectrum of the THF solution of 1, enriched with ¹³CO, at -60° C exhibited a doublet at δ 206.6 ppm (J(Rh-C) 74.0 Hz) and a double triplet at δ 193.7 ppm (J(Rh-C) 67.0 Hz, J(P-C) 15.0 Hz), in addition to a multiplet peak at δ 196.5 ppm assigned to ¹³CO in 1. The strong IR band observed at 1895 cm⁻¹ and the ¹³C NMR doublet at δ 206.6 ppm are both assigned to the mononuclear rhodate, Rh(CO)₄⁻⁻ [6]. The medium IR band at 1980 cm⁻¹, and the ³¹P{¹H} NMR and ¹³C NMR peaks at δ



Fig. 1. ³¹P{¹H} NMR and IR spectra of a THF solution of $[Rh(CO)_3P-i-Pr_3]_2$ in the presence of an excess of 1-methylimidazole. The figures in the spectra indicate the amount of added 1-methylimidazole (eq. Rh). (a), 1-methylimidazole solution of $[Rh(CO)_3P-i-Pr_3]_2$. Reaction conditions: $[Rh(CO)_3P-i-Pr_3]_2$ (25 mmol), THF (2.0 ml) and THF- d_8 (0.5 ml) at 25°C under 1 atm (CO).



Fig. 2. Plot of concentration ratio, [2]/[1], as a function of concentration of base: in DMI as solvent. (\Box) triazole; (\Box) imidazole; (\bigcirc) 1-methylimidazole; (\triangle) 1,2-dimethylimidazole; (\diamondsuit) benzimidazole; (\bigtriangledown) 1-methylimidazole; (\bigcirc) 4-dimethylaminopyridine; (\oplus) pyridine; in THF solvent, (\blacksquare) imidazole; (\bigcirc) 1-methylimidazole. Reaction conditions; $[Rh(CO)_3P-i-Pr_3]_2$, 0.2 mmol, solvent, 8 ml, 20 ° C, 1 atm (CO).

45.6(d) and 193.7(dt) ppm, respectively, were assigned to the cation [*trans*-Rh(CO)(P-i-Pr₃)₂(Im-1-Me)]⁺. The ³¹P coupling to ¹⁰³Rh (J(Rh–P) 116.8 Hz) is consistent with the four-coordinate square planar structure of rhodium(I) complexes with two phosphines *trans* to each other [7]. The double triplet pattern of the ¹³C resonance also supports this structure. Further support for these assignments is provided by the IR and ³¹P NMR data of the cationic complex [Rh(CO)(P-i-Pr₃)₂(Im-1-Me)]⁺BPh₄⁻ (3), prepared independently *, which shows absorption at 1990 cm⁻¹ and δ 46.8(d) ppm (J(Rh–P) 116.0 Hz). Thus all data seem to support the presence of the homonuclear ion pair [*trans*-Rh(CO)(P-i-Pr₃)₂(Im-1-Me)]⁺[Rh(CO)₄]⁻ (2a) in the solution.

When the solution was slightly pressurized by carbon monoxide, the intensities of the ³¹P NMR signals due to **2a** decreased, while those of the dimer complex **1** increased. Use of the ³¹P NMR data enabled us to determine the concentrations of **1** and **2a**. A plot of the ratio [2a]/[1] as a function of the concentration of free Im-1-Me gives a straight line which passes through the origin (Fig. 2).

 $[2a]/[1] = K(1/[CO]) \cdot [B]$

These results strongly suggest the reversibility of reaction 1.

We investigated the effect of a variety of nitrogen bases other than Im-1-Me on reaction 1. The IR and ³¹P NMR spectra and the conductivity of the solution, showed that **1** is converted into the ion pair **2** in the presence of an excess of base in THF. Heterocycles such as triazoles, imidazoles, and 4-aminopyridines were found to be the most effective. The equilibrium constants, K in eq. 1 for each base, measured in DMI at 25°C and calculated from the slope of the lines depicted in Fig. 2, decrease in the order; triazole (> 4.0), imidazole (3.57) > 1,2-dimethylimidazole (0.98) ~ 1-methylimidazole (0.88) > 4-dimethylaminopyridine

^{* 3} was prepared by a procedure similar to that for [Rh(CO)(P-i-Pr₃)₂(pyridine)]⁺ BPh₄⁻; see T. Yoshida, T. Okano, Y. Ueda and S. Otsuka, J. Am. Chem. Soc., 103 (1981) 3411.

(0.61) > benzimidazole (0.39 > 1-methylbenzimidazole (0.15) > pyridine (0.01). Sterically hindered 2,4,6-collidine did not cause disproportionation. Aliphatic amines, such as triethylamine, diethylamine, and 1-methylpyrrolidine, with high pKa values, yielded unidentified species which gave ³¹P NMR doublets around δ 50 ppm with J(Rh–P) 127 Hz but showed no IR absorption due to Rh(CO)₄⁻. Thus, nucleophilic attack of the base on the rhodium center, rather than simple acid–base interaction, seems to direct the disproportionation reaction of 1. Finally, it was found that in marked contrast to the ready reaction of 1, that Im-1-Me, under similar conditions, does not induce disproportionation of [Co(CO)₃P-n-Bu₃]₂ [8].

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