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CARBONYLATION OF $[Rh(COD)N_3]_2$ AND $[Rh(CO)_2NCO]_2$; A NEW SELECTIVE METHOD FOR PREPARATION OF $[Rh_6(CO)_{16}]$.

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Summary

Carbonylation of $[Rh(COD)N_3]_2$ (COD = 1, 5-cyclooctadiene) in ethanol gave the rhodium cluster $[Rh_6(CO)_{16}]$ selectively in high yield; when non polar solvents were used, the known $[Rh(CO)_2N_3]_2$ and $[Rh(CO)_2NCO]_2$ were obtained. Reaction of carbon monoxide with the isocyanato-bridged derivative $[Rh(CO)_2NCO]_2$ in ethanol also gave $[Rh_6(CO)_{16}]$. In both cases the carbonylation reaction also gave NH_2COOEt. Carbonylation of the iridium dichloride dimer $[Ir(COD)Cl]_2$ in the presence of sodium citrate gave $[Ir_4(CO)_{12}]$.

Introduction

The carbonylation of azido to isocyanato complexes in aprotic solvents is well known, and has been shown to occur readily for a number of azido-metal complexes [1–3]. Alkoxy-carbonyl derivatives have been isolated from the reaction in a protic medium [4]. The results of a study of the carbonylation in protic solvents of rhodium(I) complexes having bridged azido or isocyanato groups are described below.

Experimental

$[M(COD)Cl]_2$ (M = Rh, Ir; COD = 1,5-cyclooctadiene) were prepared as described in the literature [5,6]. The reactions were carried out under nitrogen or carbon monoxide and solvents were degassed before use. IR spectra were recorded on a Beckman 4210 instrument. Elemental analyses were performed by the Analytical Laboratory of Milan University.

$[Rh(COD)N_3]_2$

A suspension of $[Rh(COD)Cl]_2$ (1.0 g, 4.06 mmol) and NaN_3 (0.79 g, 12.5 mmol) in benzene (25 ml) was stirred at room temperature for 24 h. The yellow solution

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was filtered to remove NaCl and unreacted NaN_3 and then evaporated to dryness. The bright yellow residue was dried in vacuo.

Analyses: Found: C, 37.88; H, 4.67; N, 16.64; M.W. (benzene), 512. $[Rh(COD)N_3]_2$ calcd.: C, 37.96; H, 4.78; N, 16.60%; M.W., 506. Its IR spectrum showed absorptions at 2060 and 1275 cm^{-1} ($\nu_{as}(N_3)$ and $\nu_s(N_3)$ respectively; reported 2058 and 1279 cm^{-1}) [7].

Reaction of $[Rh(COD)N_3]_2$ *with CO in benzene*

(A) A solution of $[Rh(COD)N_3]_2$ (0.2 g) in benzene (5 ml) was treated with carbon monoxide (1 atm, 20°C) for 5 min. The insoluble wine-red product was filtered off, washed with a little benzene then n-hexane, and dried in vacuo. Its elemental analysis was consistent with the formula $[Rh(CO)_2N_3]_2$ and the IR spectrum showed the previously reported absorptions [7].

(B) When the carbonylation as in (A) is carried out for longer times (10 h) it gave a dark-red insoluble product, which was filtered off, washed with little benzene, then n-hexane, and dried in vacuo. The elemental analysis and IR data were consistent with the formula $[Rh(CO)_2NCO]_2$ [7].

Reaction of $[Rh(COD)N_3]_2$ *and* $[Rh(CO)_2NCO]_2$ *with CO in ethanol*

(1) $[Rh(CO)_2NCO]_2 + CO$. To degassed ethanol (5 ml) $[Rh(CO)_2NCO]_2$ (0.2 g) was added with stirring while CO was bubbled through. After 15 h a brown insoluble product was filtered off, washed with ethanol, then with n-hexane, and dried in vacuo. Its IR spectrum and elemental analysis were consistent with the formula $[Rh_6(CO)_{16}]$ [8] (yield: 85%). The mother liquor was evaporated to dryness and the residue treated with n-pentane; the hydrocarbon solution was filtered then evaporated to dryness, to give a residue with an IR spectrum identical with that of an authentic sample of NH_2COOEt.

(2) $[Rh(COD)N_3]_2 + CO$. The carbonylation was carried out as described in (1), but a longer time was required (24 h). The insoluble product was again shown to be $[Rh_6(CO)_{16}]$ (elemental analysis and IR data).

Reaction of $[Ir(COD)Cl]_2$ *with CO*

A methanol/water mixture (22 ml/3 ml) was treated with CO and degassed. It was refluxed, with CO bubbling through and $[Ir(COD)Cl]_2$ (0.31 g) was added with stirring. After ca. 20 min a yellow product precipitated out. A few drops of aqueous 1 *M* disodium citrate were added, and the suspension stirred for further 20 min. The yellow green product was fitered off, washed with methanol then with n-hexane, and dried in vacuo. Its IR spectrum and elemental analysis were consistent with the formula $[Ir_4(CO)_{12}]$ [9] (Yield: 61%).

Results and discussion

$[Rh(COD)N_3]_2$ was previously prepared by metathetical reaction of $[Rh(COD)Cl]_2$ with NaN_3 in benzene [7] and its reaction with CO in CH_2Cl_2 solution was reported to give $[Rh(CO)_2NCO]_2$ as the only isolable product [7]. We have found that the carbonylation of this diene complex in benzene at 1 atmosphere and room temperature leads to the isocyanato-bridged compound when long reaction times are used. By stopping the CO bubbling after few minutes, the insoluble $[Rh(CO)_2N_3]_2$

can be isolated; this derivative was previously obtained by treating $[Rh(CO)_2Cl]_2$ with NaN_3 [7]. Further treatment with CO leads to formation of $[Rh(CO)_2NCO]_2$.

Conversely, if $[Rh(COD)N_3]_2$ is carbonylated in ethanol for 24 h, the known cluster $[Rh_6(CO)_{16}]$ is formed. In this case the concomitant formation of ethylcarbamate, NH_2COOEt, is observed:

$$[Rh(COD)N_3]_2 \xrightarrow[EtOH]{CO} COD + NH_2COOEt + N_2 + [Rh_6(CO)_{16}] \qquad (1)$$

The yields of the complex are good (ca. 85%). The IR data are in agreement with those previously reported [8]. The rhodium cluster can be also obtained by carbonylation of $[Rh(CO)_2NCO]_2$ in ethanol at 1 atmosphere and room temperature for 15 h. The yields are comparable with those obtained starting from the diene complex. Formation of NH_2COOEt was again demonstrated. These results suggest that $[Rh(CO)_2NCO]_2$ is the intermediate in the formation of $[Rh_6(CO)_{16}]$ when ethanol is used as the reaction medium. Although the detailed mechanism by which $[Rh_6(CO)_{16}]$ is formed in our case is not completely clarified, we suggest that it must be quite different from that proposed for $[Rh(CO)_2Cl]_2$ as the starting material [10] because in that case HCl was shown to be produced.

The easy high-yield synthesis of the precursors, $[Rh(COD)X]_2$ ($X = Cl$, N_3), makes this procedure attractive for the preparation of the hexarhodium cluster.

The results described above were extended to the iridium analogue $[Ir(COD)N_3]_2$. Although we were unable to obtain this bridged azido derivative analytically pure, its carbonylation in ethanol produced $[Ir_4(CO)_{12}]$ (IR absorptions). We thus decided to study the carbonylation reaction of the iridium precursor $[Ir(COD)Cl]_2$ itself. The reaction of this complex with CO in methanol/water mixture at reflux gave $[Ir_4(CO)_{12}]$ in ca. 40% yield. When a base such as disodium citrate was added, the yields were raised to ca. 60%.

Work is in progress to examine the possibility of extending this process for cluster formation to other transition metals.

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