Journal of Organometallic Chemistry, 460 (1993) C34–C36

JOM 24039PC

Preliminary Communication

Disproportionation of homoleptic rhodium carbonyls

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(Received June 1, 1993)

Abstract

Both $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ disproportionate in pyridine to *cis*-$[Rh(CO)_2(py)_2]^+$ and $[Rh_5(CO)_{13}(py)_2]^-$. In the same solvent, *cis*-$[Rh(CO)_2(py)_2]^+$ is reduced by CO/H_2O to $[(py)_2H][Rh_5(CO)_{13}(py)_2]$, which has been structurally characterized.

Solutions of rhodium carbonyls in amine catalyze important reactions [1] but little is known concerning the fundamental chemistry of rhodium carbonyls in the presence of nitrogen bases. Other carbonyls of metals of Groups 8–10 have long been known to undergo disproportionation in the presence of nitrogen bases and the ionic products have been fully characterized [2]. Detailed knowledge of the chemical properties of the ions formed in the disproportionation of neutral cobalt carbonyls has been useful for understanding dihydrogen activation in the presence of bases [3]. However, there is no information available concerning the reactions with amines of the two known, stable homoleptic rhodium carbonyls, $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$.

Rapid CO evolution follows dissolution of $[Rh_4(CO)_{12}]$ in anhydrous pyridine (py) and the resulting orange solutions are conductors. In the IR spectrum of the solution (Fig. 1(a)) the highest energy band (2100 cm^{-1}) is presumably due to a cationic rhodium carbonyl complex, while the two bands at 1818 and 1756 cm^{-1} can be attributed to edge-bridging CO groups of an unknown anionic rhodium cluster. Attempts to precipitate the cation or the anion arising from the py promoted $[Rh_4(CO)_{12}]$ disproportionation invariably gave oils, and a different approach was necessary. It consisted in characterizing the anion and required a reducing agent to convert the cation into a Rh^0 carbonyl. In py, the latter disproportionated in turn, the anion finally becoming the only rhodium-containing complex in solution. This approach was suggested by the results which we had obtained treating a solution of Co^{2+} and $[Co(CO)_4]^-$ arising from the py-promoted disproportionation of $Co_2(CO)_8$ with CO/H_2 [4]. Reduction of the cation occurred and $[(py)_2H][Co(CO)_4]$ was the only cobalt-containing species. However, in the disproportionation of $[Rh_4(CO)_{12}]$ the reduction of the cation required CO/H_2O rather than CO/H_2. The addition of water to a stirred, fully disproportionated py solution of $[Rh_4(CO)_{12}]$ ($H_2O/Rh_4(CO)_{12} = 1$, molar ratio) in py under CO forms CO_2. The band at 2100 cm^{-1} disappears and those at lower frequencies increase in intensity. On addition of Et_2O, red crystals were obtained in nearly quantitative yield.

This was characterized as $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ and [pyH]Cl precipitated upon addition of LiCl to a solution in tetrahydrofuran (THF). In the ^1H NMR spectrum (THF-d_8) the resonances between 7 and 9 ppm (18.5 H) of the pyridine rings were accompanied by a resonance at 15.13 ppm (1 H), attributed to H^+ of the cation. During refinement of the solid state structure *, two molecules of non-Rh-coordinated py were resolved for each $Rh_5(CO)_{13}(py)_2$ unit using difference Fourier maps. While it was impossible to distinguish between C and N atoms, a short distance of 2.518 Å between two vertices of the two six-membered rings indicated a hydrogen bond between the pyridine molecules [5]. The molecular structure of the anion is shown in Fig. 2. The five Rh atoms are at the vertices of a trigonal bipyramid. There are seven terminal and six edge-bridging carbonyls, three spanning the equatorial plane, in addition to those bridging Rh1–Rh5, Rh2–Rh3 and Rh3–Rh4. The two coordinated py molecules are bonded to Rh3. The structure of

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* Crystal data: Measurements were made at room temperature on a Philips PW1100 single-crystal diffractometer equipped with graphite monochromatized Mo-Kα radiation ($\lambda = 0.7107$ Å). $[(py)_2H][Rh_5(CO)_{13}(py)_2]$, $C_{33}H_{21}N_4O_{13}Rh_5$, $M = 1195.5$, monoclinic, space group $P2_1/a$, $a = 20.137(3)$, $b = 21.131(3)$, $c = 18.763(3)$ Å; $\beta = 103.81(2)°$. $V = 7753.1$ Å^3, $Z = 8$, $D_{calc} = 2.046$ g cm^{-3}, μ(Mo-Kα) = 20.5 cm^{-1}, $F(000) = 5280$. $R = 0.053$ and $Rw = 0.061$ for 372 parameters and 4731 reflections [$I > 3\sigma(I)$] measured in the range $0 < \theta < 20°$.

0022-328X/93/$6.00

$[Rh_5(CO)_{13}(py)_2]^-$ can be compared with that of the isoelectronic $[Rh_5(CO)_{15}]^-$ [6]. The replacement of two carbonyls by two py molecules produces one more edge-bridging carbonyl but other structural features are unaltered. Likewise, in $[Rh_5(CO)_{15}]^-$ the average of the Rh–Rh distance in the equatorial plane (2.697 Å) is considerably shorter than the average of Rh–Rh distance involving the axial rhodium atoms (2.971 Å).

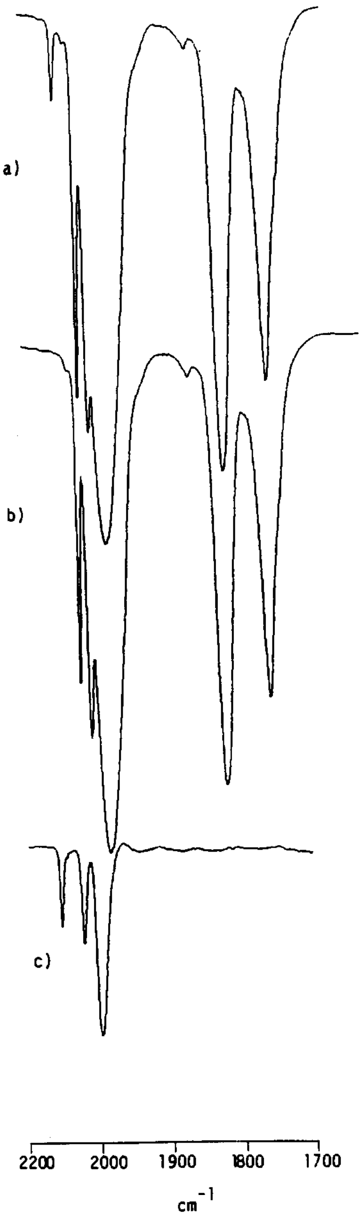


Fig. 1. (a) IR spectrum of a fully disproportionated 0.02 M py solution of $[Rh_4(CO)_{12}]$ (p_{CO} = 735 Torr); (b) IR spectrum of a 0.0133 M py solution of $[(py)_2H][Rh_5(CO)_{13}(py)_2]$; (c) (a) – (b) difference spectrum.

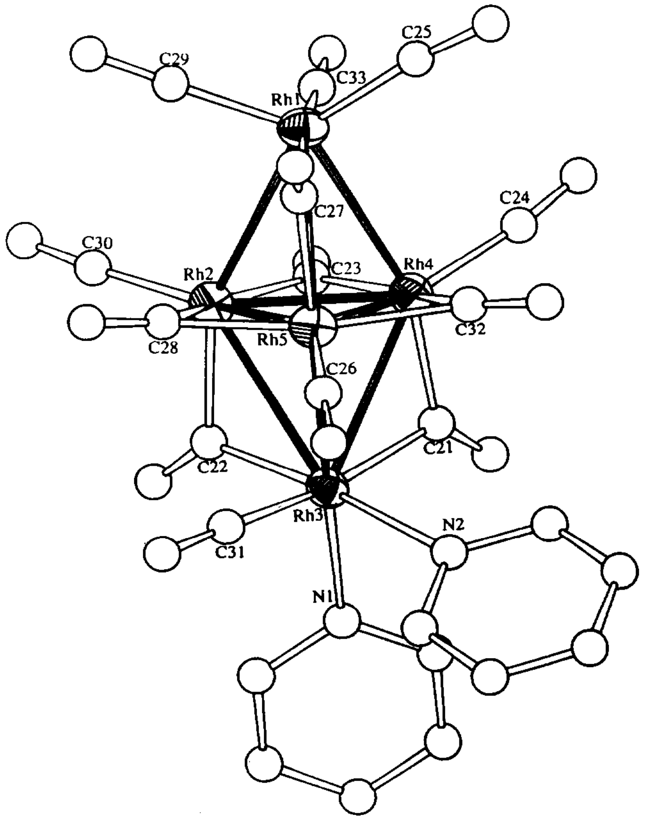


Fig. 2. Molecular crystal structure of $[Rh_5(CO)_{13}(py)_2]^-$. Important molecular parameters (Å and °): Rh1–Rh2 3.005(2), Rh1–Rh4 3.005(3), Rh1–Rh5 2.908(2), Rh2–Rh3 3.002(3), Rh2–Rh4 2.664(3), Rh2–Rh5 2.711(3), Rh3–Rh4 2.952(2), Rh3–Rh5 2.954(3), Rh4–Rh5 2.716(3), Rh3–N1 2.249(11), Rh3–N2 2.205(9), Rh2–C22 2.013(15), Rh3–C21 2.068(16), Rh3–C22 1.999(18), Rh3–C31 1.912(17), Rh4–C21 1.964(15); Rh2–C22–Rh3 96.9(6), Rh3–C21–Rh4 94.1(6), N1–Rh3–N2 85.1(3), N1–Rh3–C21 88.7(4), N1–Rh3–C22 174.0(4).

The IR spectrum of $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ in the CO stretching region is the same both in the solid state and in py solution (Fig. 1(b); ν_{CO} = 2040m, 2011m, 1980vs, 1818m, 1756m cm^{-1}), showing that the anion $[Rh_5(CO)_{13}(py)_2]^-$ retains its structure in both phases. All the absorptions due to this anion can be detected in a fully disproportionated solution of $[Rh_4(CO)_{12}]$ in anhydrous pyridine, together with the band at 2100 cm^{-1} of the rhodium countercation. The IR spectrum of the rhodium cation remained when the absorptions of a 0.0133 M py solution of $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ were subtracted to those of a fully disproportionated 0.020 M solution of $[Rh_4(CO)_{12}]$ in the same solvent. Three bands (2100m, 2038m and 1993s, cm^{-1}) resulted when a solution of $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ was kept under CO (Fig. 1(c)); under argon it reversibly converted into a single band spectrum (1993 cm^{-1}), suggesting that the rhodium cation is actually an equilibrium mixture of *cis*-$[Rh(CO)_2(py)_2]^+$ (2100m and 2038m cm^{-1}) and $[Rh(CO)(py)_3]^+$ (1993 cm^{-1}). Separate experiments confirmed that preformed *cis*-$[Rh(CO)_2(py)_2]^+$, PF_6^- or BPh_4^- salt [7], loses CO

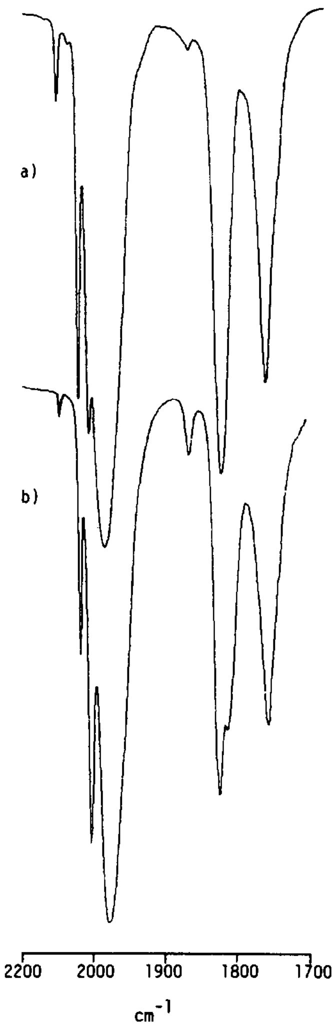
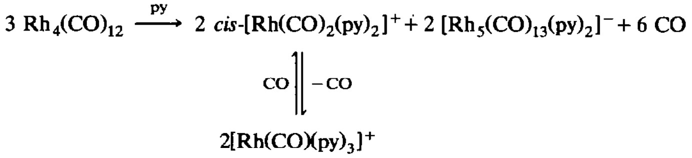


Fig. 3. Comparison between the IR spectra of a fully disproportionated 0.02 M solution of $[Rh_4(CO)_{12}]$ in different media: (a) in py; (b) in THF containing 1% en.

reversibly in py. The three bands were again obtained under CO, while the single band (1993 cm^{-1}) was observed under Ar. A gas-volumetric measurement gave a value of 1.55 for the ratio $[Rh(CO)(py)_3]^+/[cis\text{-}Rh(CO)_2(py)_2]^+$, at $p_{CO} = 735$ Torr at 30°C.

$$cis\text{-}[Rh(CO)_2(py)_2]^+ + py \rightleftharpoons [Rh(CO)(py)_3]^+ + CO \quad (1)$$

Based on these findings, the py promoted disproportionation of $[Rh_4(CO)_{12}]$ can be formulated as in eqn. (2).



$$\begin{array}{c} 3\,Rh_4(CO)_{12} \xrightarrow{py} 2\,cis\text{-}[Rh(CO)_2(py)_2]^+ + 2\,[Rh_5(CO)_{13}(py)_2]^- + 6\,CO \\ CO\,\Big\Updownarrow\,-CO \\ 2[Rh(CO)(py)_3]^+ \end{array} \quad (2)$$

The stoichiometry of this reaction was confirmed by a gas-volumetric measurement. 2.38 mmols of CO per mmol of $[Rh_4(CO)_{12}]$ were evolved on dissolving the neutral carbonyl in py at 30°C at $p_{CO} = 735$ Torr. A $CO/[Rh_4(CO)_{12}]$ molar ratio of 2 is obtained by correcting to this value with the CO evolved according to equilibrium (1).

The same ions, $[Rh_5(CO)_{13}(py)_2]^-$ and *cis*-$[Rh(CO)_2(py)_2]^+$, are formed from the py-promoted disproportionation of $[Rh_6(CO)_{16}]$: an IR spectrum superimposable on that of Fig. 1(a) was obtained on stirring a solution of $[Rh_6(CO)_{16}]$ in py for three h under CO at room temperature. Moreover, IR spectroscopic evidence indicates that in a THF solution moderate amounts of ethylenediamine (en) promotes the disproportionation of both $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$. The IR spectrum of the solution resulting from the py-induced disproportionation of $[Rh_4(CO)_{12}]$ and that of the solution resulting from the en-promoted disproportionation in THF is represented in Fig. 3. The similarity between them suggests the formation of $[Rh_5(CO)_{13}(en)]^-$ and *cis*-$[Rh(CO)_2(en)]^+$, the en substituting two py molecules.

We are presently investigating whether and to what extent the reduction of *cis*-$[Rh(CO)_2(py)_2]^+$ to CO_2 and $[(py)_2H][Rh_5(CO)_{13}(py)_2]$ by CO/H_2O is relevant to the WGSR promoted by amine solutions of rhodium carbonyls [1].

Acknowledgements

We thank Dr. G. Fochi and Dr. F. Marchetti for helpful discussions, Mr. F. Dei Cima for technical assistance, Ministero della Ricerca Scientifica e Tecnologica (MURST) for financial support and Chimet S.p.a. for a loan of rhodium.

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