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$Co_2(CO)_8$-promoted dihydrogen activations under unusually mild conditions by highly polarizing Co^{2+} cations

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Abstract

The reaction between $Co_2(CO)_8$ and CoX_2 ($X = Cl$, I, $O_2CC_2H_5$) in THF involves in a P(CO)-dependent disproportionation of the neutral carbonyl:

$$\tfrac{3}{2}Co_2(CO)_8 + CoX_2 \rightleftarrows 2[Co(CO)_4]^- + 2[CoX]^+ + 4CO$$

For $X^- = I^-$, a stable Co^{II}, Co^{-I} homonuclear ion-pair (HNIP) is the only product at room temperature, while for $X^- = Cl^-$ and $O_2CC_2H_5^-$ the free $[Co(CO)_4]^-$ is also formed. For $X = Cl^-$ or $O_2CC_2H_5^-$ the solutions obtained activate dihydrogen under unusually mild conditions; highly polarizing Co^{2+} cations, insufficiently stabilized by $[Co(CO)_4]^-$ and the X ligand, are suggested to be the active species in this activation. This picture would also account for the catalytic effect of small amounts of pyridine on the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and dihydrogen in toluene.

Introduction

The reaction of H_2 and $Co_2(CO)_8$ to give $HCo(CO)_4$ is believed to be a key step in cobalt-catalyzed hydroformylation. The most widely accepted mechanism for the reaction in hydrocarbons is that proposed by Ungváry [1], in which oxidative addition of H_2 to $Co_2(CO)_7$ is the slow step. However, alternative pathways of lower energies may exist since the reaction is greatly accelerated by small amounts of py (py = pyridine) in toluene [2]; this base effect remains unexplained. Subsequently, it was suggested [3,4] that homonuclear ion pairs (HNIP) may be involved in dihydrogen activation promoted by $Co_2(CO)_8$ in presence of small amounts of base. Such HNIP are formed by the disproportionation of neutral metal carbonyls in the presence of small amounts of fairly strong bases in low dielectric constant solvents. The tetra-HNIP $[(py)_2FeFe(CO)_4]_2$ has been isolated from $Fe(CO)_5$ and py [5] and $[(py)_3CoCo(CO)_4][Co(CO)_4]$ and $[\{Co_3(CO)_{10}\}_2\{Co(py)_4\}]$ have been

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isolated from the reaction of $Co_2(CO)_8$ and small amounts of py in hydrocarbons [6]. In THF (THF = tetrahydrofuran) as solvent, the Fe^{II}, Fe^{-II} HNIP is stable, while the Co^{II}, Co^{-I} HNIP are in equilibrium [4] with the corresponding free ions (eq. 1).

$$\tfrac{3}{2}Co_2(CO)_8 \overset{\text{THF, py}}{\rightleftarrows} 4\,CO + Co^{II},Co^{-I}\ \text{HNIP} \rightleftarrows 2[Co(CO)_4]^- + Co^{2+} \qquad (1)$$

The lower stability of the cobalt-HNIP is due to the fact that the charge of $[Co(CO)_4]^-$ is lower than that of $[Fe(CO)_4]^{2-}$.

THF, py and the poorly coordinating $[Co(CO)_4]^-$ anions compete for the coordination sphere of Co^{2+} cations. Such Co^{2+} cations display oxidizing properties, so that with increase in $P(CO)$, the $[Co(CO)_4]^-$ anions are converted back into $Co_2(CO)_8$, the value of $E°_{\frac{1}{2}}(Co_2(CO)_8/[Co(CO)_4]^-)$ being +0.4 V [7]. In the presence of CO, dihydrogen is also oxidized by such Co^{2+} cations under unusually mild conditions [4] (eq. 2).

$$Co^{2+} + \tfrac{3}{2}H_2 \xrightarrow[20\,°C,\ 1\ \text{atm}]{\text{THF, py, CO}} 3[py_2H]^+ + [Co(CO)_4]^- \qquad (2)$$

We now report that the Co^{2+} cations involved in equilibria such as 1 behave as active species in $Co_2(CO)_8$-promoted dihydrogen activation occurring under unusually mild conditions.

Results and discussion

The behaviour of $[py_2H][Co(CO)_4]$ in solution. $[py_2H][Co(CO)_4]$, formed on dihydrogen oxidation promoted by Co^{2+} cations (eq. 2), was obtained in quantitative yields following sublimation as orange crystals by direct combination at −70 °C of py and preformed $HCo(CO)_4$ in n-hexane. The compound is stable both as solid and in the THF solution; in both cases only the IR absorption of unperturbed $[Co(CO)_4]^-$ is observed. However, the IR spectrum of a freshly prepared 0.016 *M* toluene solution of $[py_2H][Co(CO)_4]$ is much more complicated, as shown in Fig. 1 The weak band at 2110 cm^{-1} indicates the presence of $HCo(CO)_4$, while the absorptions at 2010, 1934 and 1902 cm^{-1} duplicate, in wavenumber and intensities, those of the trialkylamine adducts of $HCo(CO)_4$, for which preferential tight ion pairing $R_3NH...(OC)_3CoCO$ has been demonstrated [8,9*]. The IR absorptions of $HCo(CO)_4$ (2110w, 2040s, 2010vs cm^{-1}) were more clearly observed in a distilled portion of the solution. All three species in equilibrium 3 are thus present in toluene, although only free $[Co(CO)_4]^-$ is present in THF.

$$[py_2H][Co(CO)_4] \underset{+py}{\overset{-py}{\rightleftarrows}} pyH...(OC)_3CoCO \underset{+py}{\overset{-py}{\rightleftarrows}} HCo(CO)_4 \qquad (3)$$

On the basis of reactions 2 and 3, it can be seen that in toluene the $HCo(CO)_4$ can be a product of dihydrogen oxidation promoted under unusually mild conditions by Co^{2+} cations insufficiently stabilized by bases. Accordingly, Scheme 1 accounts for

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* Reference number with asterisk indicates a note in the list of references.

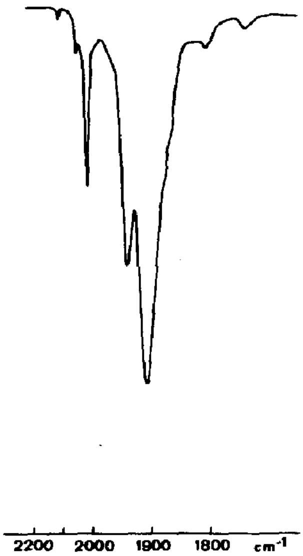
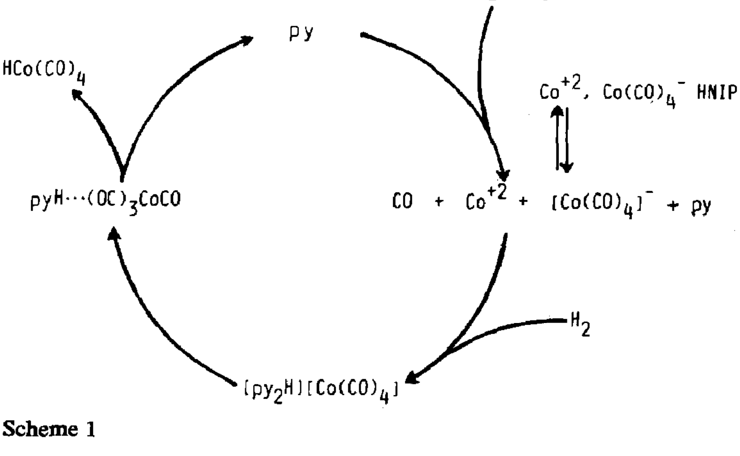


Fig. 1. The IR spectrum of a 0.016 *M* toluene solution of $[py_2H][Co(CO)_4]$.

the catalytic effect [2] of small amounts of py on $HCo(CO)_4$ formation from $Co_2(CO)_8$ and H_2 in toluene.

The autocatalytic synthesis of $Co_2(CO)_8$ *from cobalt(II) dicarboxylates and synthesis gas.* The synthesis of $Co_2(CO)_8$ from cobalt(II) dicarboxylates and synthesis gas is known to require drastic conditions and to be autocatalytic [10]. In keeping with this we have found that $Co_2(CO)_8$ is formed even at room temperature and under one atmosphere of synthesis gas in solutions containing equimolar amounts of cobalt(II) dipropionate and $Co_2(CO)_8$. The usual explanation for the autocataly-



Scheme 1

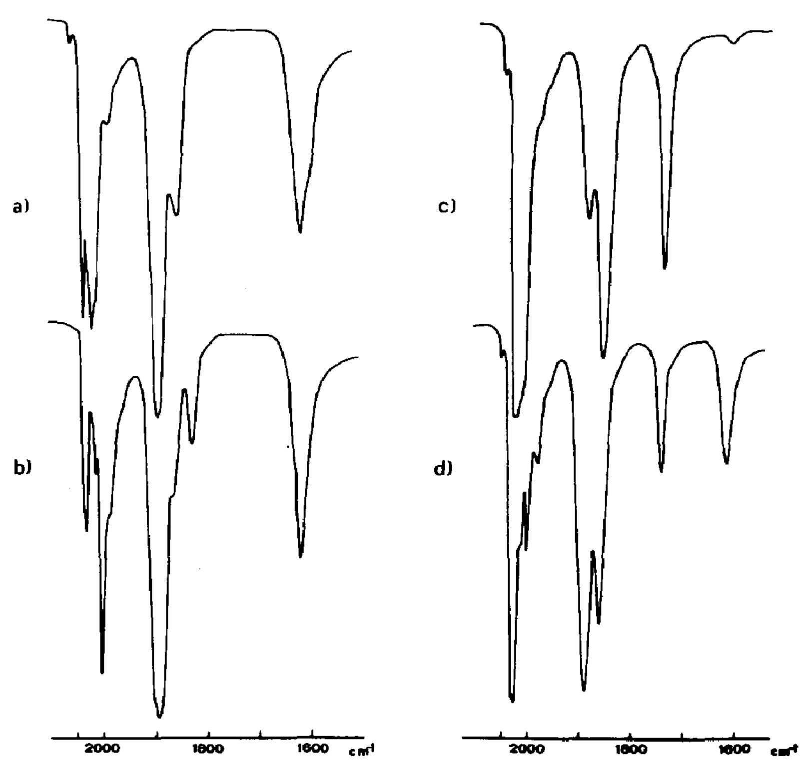


Fig. 2. IR spectra of a 0.03 *M* THF solution of $Co_2(CO)_8$ after addition of equimolar amounts of $Co(O_2CC_2H_5)_2$ and equilibrated under various P(CO) and $P(H_2)$. (a) $P(H_2)$ 0, P(CO) 600 mmHg; (b) $P(H_2)$ 0, P(CO) 10 mmHg; (c) $P(H_2) = P(CO) = 300$ mmHg; (d) $P(H_2)$ 300 mmHg, P(CO) 90 mmHg.

sis involves as the slow step the formation of $HCo(CO)_4$, according to the following sequence [11]:

$$Co_2(CO)_8 + H_2 \xrightarrow{\text{slow}} 2HCo(CO)_4$$

$$2HCo(CO)_4 + CoR_2 \xrightarrow{\text{fast}} \{Co[Co(CO)_4]_2\} + 2RH$$

$$\{Co[Co(CO)_4]_2\} + 4CO \xrightarrow{\text{fast}} \tfrac{3}{2}Co_2(CO)_8$$

(R = 2-ethylhexanoate)

Another possibility involved the direct interaction of cobalt(II) dipropionate and $Co_2(CO)_8$ in THF. We therefore examined by gas volumetric measurement and IR spectroscopy the behaviour of a THF solution 0.03 *M* in both cobalt(II) propionate and $Co_2(CO)_8$. The extent of the reaction was found to depend on P(CO) as shown by the spectra of the solution at two P(CO)'s (600 and 10 mmHg, respectively, Fig. 2a and 2b). At P(CO) 600 mmHg, the IR spectrum reveals the presence of unchanged $Co_2(CO)_8$ together with free $[Co(CO)_4]^-$ (ν(CO) 1887 cm^{-1}), while the broad band at 1618 cm^{-1} is due to propionate coordinated to Co^{II}. At P(CO) 10 mmHg, small amounts of $Co_4(CO)_{12}$ can be detected (ν(CO) 2066, 2054 and 1858 cm^{-1}), and there are absorptions at 2003 and 1823 cm^{-1} due to the anionic cluster

$[Co_3(CO)_{10}]^-$ [12]. On these grounds, the reaction between $Co_2(CO)_8$ and cobalt(II) dipropionate can be formulated as in eq. 4.

$$\tfrac{3}{2}Co_2(CO)_8 + Co(O_2CC_2H_5)_2 \overset{THF}{\rightleftharpoons} 2[Co(CO)_4]^- + 2[CoO_2CC_2H_5]^+ + 4\,CO \qquad (4)$$

Equilibrium 5, separately studied in ethereal tetracarbonylcobaltate/cobalt carbonyls solutions [13], is also present simultaneously in the solution.

$$Co_2(CO)_8 + [Co(CO)_4]^- \underset{+2\,CO}{\overset{-2\,CO}{\rightleftharpoons}} [Co_3(CO)_{10}]^- \rightleftharpoons \tfrac{1}{2}Co_4(CO)_{12} + [Co(CO)_4]^- \qquad (5)$$

As a consequence of reaction 4, treatement of $Co(O_2CC_2H_5)_2$ with $Co_2(CO)_8$ lowers the number of charged propionate ligands available for Co^{II}. The electroneutrality of the solution is retained through the formation of $[Co(CO)_4]^-$ and $[Co_3(CO)_{10}]^-$, each of which is a poorly coordinating anion. In this way Co^{2+} cations insufficiently stabilized by ligands are formed; we shall see that, in the presence of CO, such cations promote dihydrogen oxidation under unusually mild conditions, just as $[Co(CO)_4]^-$ anions are oxidized back to $Co_2(CO)_8$ on increasing $P(CO)$ (reaction 4).

The above mentioned solution of cobalt(II) propionate and $Co_2(CO)_8$ reacts with dihydrogen at room temperature and atmospheric pressure. The IR spectrum of Fig. 2c was observed after 8 h at 25 °C under $P(CO) = P(H_2) = 300$ mmHg. The broad band at 1618 cm^{-1} of propionate was reduced in intensity while a band at 1743 cm^{-1}, due to propionic acid had appeared; the concentration of neutral cobalt carbonyls had increased, showing that cobalt(II) dipropionate has been converted into $Co_2(CO)_8$ and $Co_4(CO)_{12}$. According to equilibrium 4, the 1887 cm^{-1} band of $[Co(CO)_4]^-$ strongly decreases in intensity as a consequence of the fallen concentration of the propionate base. The reaction was found to be reversible and the redox equilibrium 6 can therefore be formulated:

$$2Co_2(CO)_8 + 2C_2H_5COOH \overset{THF}{\rightleftharpoons} H_2 + 2[CoO_2CC_2H_5]^+ + 2[Co(CO)_4]^- + 8\,CO \qquad (6)$$

In accord with this, we found that addition of propionic acid to THF solutions of $Co_2(CO)_8$ brought about CO/H_2 evolution in 8.2/1 molar ratio.

Equilibrium 6 was confirmed by studying the effect of $P(CO)$. The 1/1 $Co(O_2CC_2H_5)_2/Co_2(CO)_8$ solution described above was equilibrated under a constant $P(H_2)$ 300 mmHg at a lower $P(CO)$ 90 mmHg. The IR spectrum of the resulting solution is shown in Fig. 2d, and can be compared with that of Fig. 2c. Comparison of the relative intensities of the bands due to propionate (1618 cm^{-1}) and to propionic acid (1743 cm^{-1}) in the two spectra shows that on lowering $P(CO)$ the acidic hydrogen of propionic acid is reduced to dihydrogen; the contrary change occurs on increasing $P(CO)$. No IR absorptions due to HNIP can be detected in either Fig. 2c or 2d. These results suggest that the highly polarizing CoL_n^{2+} cations involved in equilibrium 4 are the active species in dihydrogen oxidation under such mild conditions.

The $CoCl_2/Co_2(CO)_8$ promoted dihydrogen activations. $HCo(CO)_4$ always accompanies $Co_2(CO)_8$-promoted dihydrogen activation, so that it has been believed to be a "quintessential catalyst" [14], a necessary intermediate. This assumption has

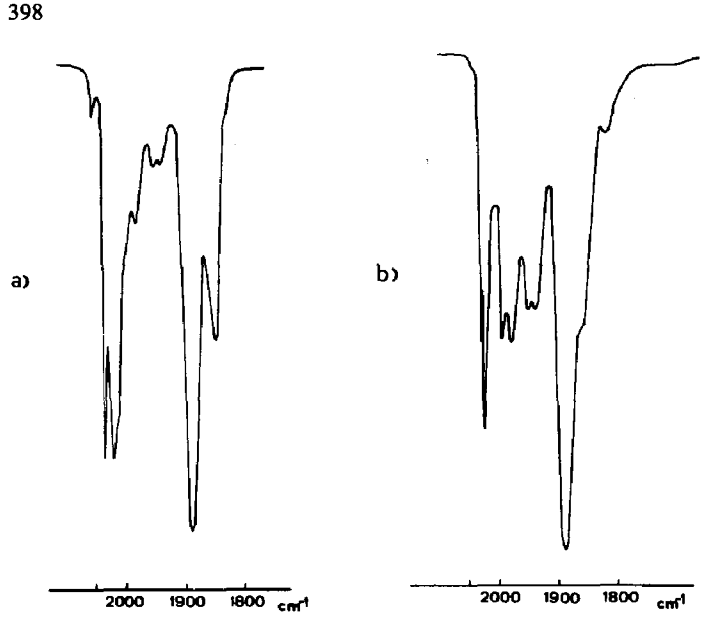


Fig. 3. IR spectra of a 0.03 *M* THF solution of $Co_2(CO)_8$ after addition of equimolar amounts of $CoCl_2$ and equilibrated under (a) *P*(CO) 600 and (b) *P*(CO) 10 mmHg.

never been tested for the $Co_2(CO)_8$ promoted dihydrogen activations which occur under mild conditions and which can be related to the reversible disproportionation of $Co_2(CO)_8$. In fact, during the two dihydrogen activations described above (reactions 2 and 6), $HCo(CO)_4$ was never detected, a possible explanation being its deprotonation by py or propionate base. The same explanation, however, cannot be applied to two cases of dihydrogen activation under unusually mild conditions reported in the present section, in which chloride ions were used as the base in order to promote the reversible disproportionation of $Co_2(CO)_8$.

The IR spectra of a THF solution 0.03 *M* both in $Co_2(CO)_8$ and $CoCl_2$, equilibrated under *P*(CO) 600 and 10 mmHg are shown in Fig. 3a and 3b, respectively. An intermediate situation, *P*(CO) 300 mmHg (and $P(H_2)$ 300 mmHg), is shown in Fig. 4a. Under *P*(CO) 10 mmHg the bands due to free $[Co(CO)_4]^-$ (1887 cm^{-1}), $[Co_3(CO)_{10}]^-$ (2003 and 1823 cm^{-1}), and $Co_4(CO)_{12}$ (2066, 2054 and 1858 cm^{-1}) are observed, while the bands at 2055, 1978, 1950 and 1938 cm^{-1} can be attributed to a Co^{II}, Co^{-I} HNIP (presumably tetranuclear, see below). At *P*(CO) 600 mmHg, all the absorptions due to anionic carbonylmetalates and to the HNIP are of reduced intensity, and the neutral carbonyl $Co_2(CO)_8$ is formed. The reaction between $Co_2(CO)_8$ and $CoCl_2$ in THF can therefore be formulated as in eq. 7.

$$\tfrac{3}{2}Co_2(CO)_8 + CoCl_2 \overset{THF}{\rightleftharpoons} 2[Co(CO)_4]^- + 2[CoCl]^+ + 4\,CO \qquad (7)$$

Equilibrium 7 is present along with equilibrium 5 and Co^{II}, Co^{-I} HNIP equilibria. Like $Co(O_2CC_2H_5)_2$, $CoCl_2$ promotes a reversible disproportionation of $Co_2(CO)_8$, and in consequence the ratio between chloride ligands and Co^{2+} cations falls to values of < 2. Thus, by the operation of equilibrium 7, $CoCl_2$ generates highly polarizing Co^{2+} cations, insufficiently stabilized by chloride ligands.

Such cations are expected to promote dihydrogen activation under very mild conditions. Indeed the above mentioned $Co_2(CO)_8/CoCl_2$ solution was found to

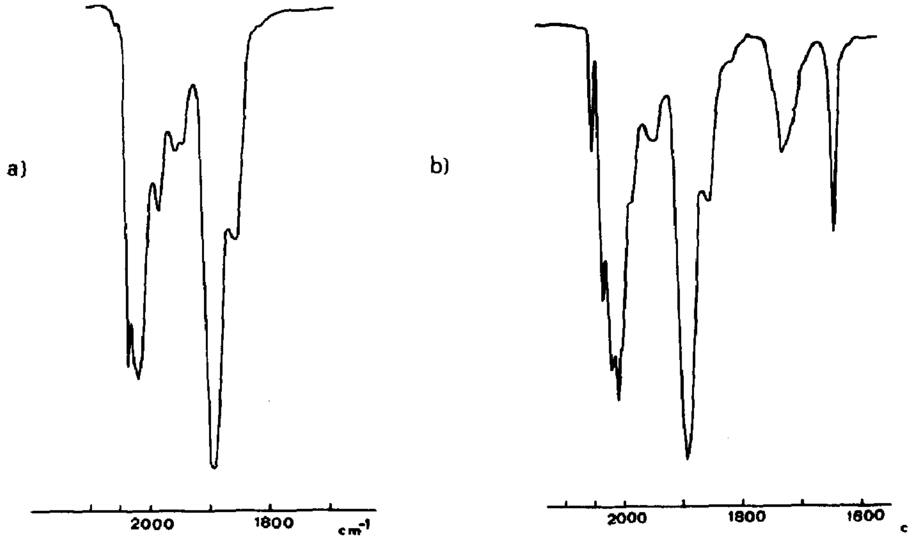


Fig. 4. IR spectra of a THF solution 0.03 *M* both in $Co_2(CO)_8$ and $CoCl_2$ (a) equilibrated under $P(CO) = P(H_2)$ 300 mmHg; (b) after 15 h reaction with CO, H_2 and 1-hexene.

promote fast H_2–D_2 scrambling at room temperature and under $P(CO) = P(H_2) + P(D_2) = 300$ mmHg. In these solutions IR absorptions due to $HCo(CO)_4$ were never observed; moreover $HCo(CO)_4$ has been found to be inactive in promoting H_2–D_2 scrambling [15], so that $HCo(CO)_4$ cannot be invoked as an intermediate. IR bands of $HCo(CO)_4$ were also not observed when 30 ml of the 1/1 $CoCl_2/Co_2(CO)_8$ 0.03 *M* THF solution were equilibrated under $P(CO) = P(H_2)$ 300 mmHg (Fig. 4a). However when 2.4 ml of 1-hexene was added to the solution, gas absorption took place and the bands due to acylcobalt tetracarbonyls [16] appeared in the IR spectrum (2104m, 2042vs, 2021vs, 2001m, 1710w cm^{-1}, Fig. 4b). The reaction proceeds in an analogous way, at comparable rates, to that induced by small amounts of water in a THF 0.03 *M* $Co_2(CO)_8$ solution [3]. With long times of reaction (one day or more) the acyls groups were slowly hydrogenated to C_7 aldehydes (normal/branched/internal = 4/4/1). The requirement for the formation of acylcobalt tetracarbonyls under so mild conditions seems to be the presence of highly polarizing Co^{2+} cations insufficiently stabilized by ligands, and these cations appear to promote H_2, 1-hexene and CO activations according to eq. 8.

$$Co^{2+} + 2Co(CO)_4^- + \tfrac{1}{2}H_2 + 5\ CO + \text{1-hexene} \xrightarrow{22°C;\ 1\ atm} Co_2(CO)_8 + C_6H_{13}C(O)Co(CO)_4 \quad (8)$$

The experiments in the following section offer additional evidence for the importance of this requirement.

The properties of $CoI_2/Co_2(CO)_8$ solutions. The reversible disproportionation of $Co_2(CO)_8$ is known to be induced by neutral (H_2O, py [3] [4]) and charged ($C_2H_5CO_2^-$, Cl^- [this paper]) bases, and in consequence of this, reversible dihydrogen activation can occur under unusually mild conditions. However, we found that the charged base I^- promoted a reversible disproportionation but not a corresponding dihydrogen activation: neither H_2–D_2 scrambling nor acylcobalt tetracarbonyls formation from 1-hexene and synthesis gas occurs at room temperature and atmospheric pressure in a 0.03 *M* THF solution of $Co_2(CO)_8$ containing equimolar amounts of CoI_2. According to our proposals, regarding highly polarizing Co^{2+} cations insufficiently stabilized by bases as the active species in promoting dihydrogen activation, this means that such cations are not formed as products of the CoI_2-promoted $Co_2(CO)_8$ disproportionation. In fact, the IR spectra of the $CoI_2/Co_2(CO)_8$ solution differ strikingly from those of the previous cases: as can be seen in Fig. 5a, b and c, under *P*(CO) 600, 300, and 10 mmHg the 1887 cm^{-1} band of unperturbed $[Co(CO)_4]^-$ is always absent. Instead, four bands (2055s, 1978s, 1950vs and 1938vs cm^{-1}) at higher frequences suggest the presence of Co^{II}, Co^{-I} HNIP associated through metal–metal covalent bonds [17]. To confirm this a THF solution in which these absorptions are the only ones detectable (Fig. 6a) was obtained as described in the Experimental section and examined by IR spectroscopy in 240–298 K temperature range. All four bands were found to change in intensity in a parallel way on varying the temperature (Fig. 6b and c), and at low temperatures the 1887 cm^{-1} band of free $[Co(CO)_4]^-$ becomes evident. The analogy between the spectrum of this HNIP and that of $[(py)_2FeFe(CO)_4]_2$ [5] prompts us to propose a tetranuclear form of HNIP $[(THF)_nICoCo(CO)_4]_2$, which at room temperature is the only product of the CoI_2-promoted disproportionation of $Co_2(CO)_8$ (eq. 9).

$$\tfrac{3}{2}Co_2(CO)_8 + CoI_2 \overset{THF}{\rightleftharpoons} [(THF)_nICoCo(CO)_4]_2 + 4CO \qquad (9)$$

On this view the absence of dihydrogen activation by $CoI_2/Co_2(CO)_8$ THF solutions can be related to the favourable combination of I^-, $[Co(CO)_4]^-$ and THF as ligands for Co^{2+} cations. Apparently the formation of Co^{II}, Co^{-I} HNIP of relatively high stability can preclude the presence of the highly polarizing Co^{2+} cations

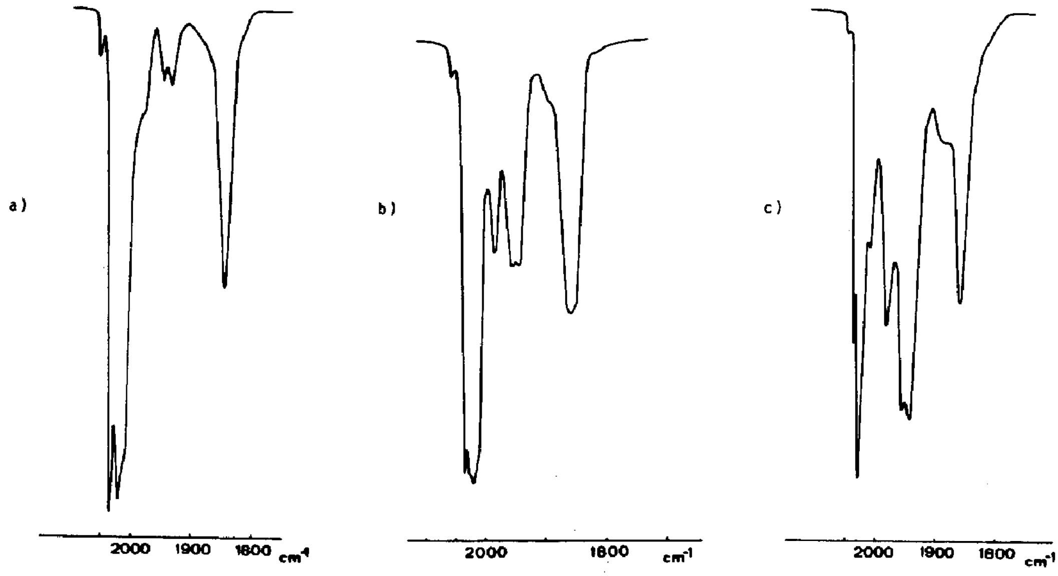


Fig. 5. IR spectra of a 0.03 *M* THF solution of $Co_2(CO)_8$ after addition of equimolar amounts of CoI_2 and equilibration under (a) *P*(CO) 600 mmHg; (b) *P*(CO) = *P*(H_2) 300 mmHg; and (c) *P*(CO) 10 mmHg.

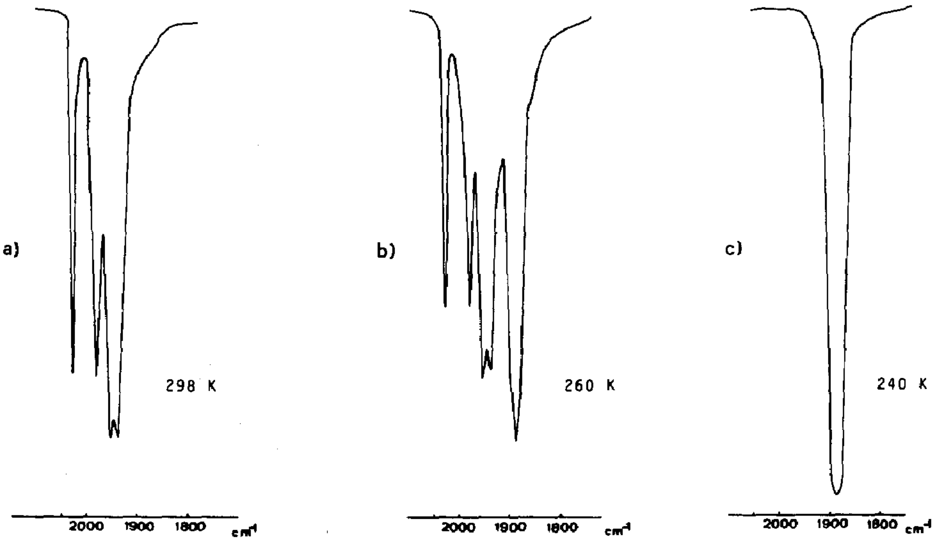


Fig. 6. IR spectra of $[(THF)_nICoCo(CO)_4]_2$ in THF, 240–298 K, Ar atmosphere.

insufficiently stabilized by bases which are the active species in dihydrogen activation under mild conditions.

The present results indicate that in several cases dihydrogen activation promoted by cobalt carbonyls can be related to their CO-dependent disproportionation induced by a large variety of neutral and charged bases. Highly polarizing Co^{2+} cations that are insufficiently stabilized by bases appear to be the active species. Nevertheless, the detailed mechanism of such dihydrogen activation under unusually mild conditions remains to be elucidated. Kinetic measurements on such complicated systems would be extremely difficult, but the nature of the active species suggests heterolytic splitting of the dihydrogen [18].

Experimental

General. All manipulations were carried out under prepurified argon by standard Schlenk techniques. Liquid samples for infrared spectra were taken with a syringe and transferred to a 0.1 mm CaF_2 cell. The IR spectra were recorded on a Perkin–Elmer model 283 instrument, and the IR absorptions of the solvent were compensated by placing in the reference beam a 0.1 mm CaF_2 cell filled with pure solvent. Variable temperature measurements were carried out in a 0.1 mm CaF_2 cell, part of a Specac apparatus supplied by Analytical Accessories Limited, Orpington, Kent (England). Analyses of gases were performed with a Dani model 3200 gas chromatograph equipped with HWD detector and a molecular sieve column (argon as carrier gas). Mass spectra of H–D mixtures were performed with a V. G. Analytical, model 70-70 E mass spectrometer. Gas chromatographic analyses of C_7 aldehydes were performed using a Hewlett–Packard model 5700 A equipped with a FID detector and a Carbowax 20M column. Quantitative determination of py was performed by gas chromatographic comparison (Fractovap 2450 apparatus with HWD detector) with standards; samples were treated with KOH in CH_3OH before analysis. Quantitative analyses for cobalt were performed with aqueous Co^{2+} solutions by the complexometric method (EDTA; PAN). The aqueous Co^{2+} solutions were obtained by treatment of samples with I_2/CH_3OH followed by addition of 1/1 aqueous HNO_3. Clear pink solutions were obtained on boiling. Quantitative analyses of CO were performed measuring gas evolved on treatment of samples with I_2/py.

$Co_2(CO)_8$ was purchased from Strem Chemicals and sublimed (38° C, 0.1 mmHg). $Co(O_2CC_2H_5)_2$ was prepared from $CoCO_3$ and C_2H_5COOH [19]. Anhydrous $CoCl_2$ was obtained by refluxing the hexahydrate form (Carlo Erba Co.) in $SOCl_2$. CoI_2 in graphite-like form (see: Gmelins Handbuch der Anorganischen Chemie, Verlag Chemie, Weinheim, Germany, 1961; Vol.58/A, p 595) was obtained in quantitative yields by addition of stoichiometric amounts of iodine to a toluene solution of $Co_2(CO)_8$. The solid precipitates was filtered off, washed twice with toluene, and dried under vacuum. Anal. Found: Co, 18.75; I, 81.10. CoI_2 calcd.: Co, 18.86; I, 81.14%. H_2, CO and a 1/1 mixture thereof as pure gases were supplied by Rivoira Co. A mixture of $CO/H_2/Ar$ 1/3.3/2.3 was supplied by SOL Co.

Preparation of $[py_2H][Co(CO)_4]$. A 0.19 *M* n-hexane solution of $HCo(CO)_4$ was obtained on adding 500 ml HCl (25° C, 1 atm.; 20.4 mmol) by a syringe, through a rubber septum, to a stirred suspension of 3.65 g (20.5 mmol) of $LiCo(CO)_4$ [20] in 100 ml of n-hexane at −40° C. The temperature was raised to 0° C and the volatile components of the suspension distilled off under vacuum. An aliquot of the distillate was titrated potentiometrically against NaOH 0.1 *N*. 2.8 ml of py (34.7 mmol) were added on stirring at −70° C, to 90 ml of the 0.19 *M* n-hexane $HCo(CO)_4$ solution (17.1 mmol). A white precipitate, turning orange at room temperature, was immediately formed, and was filtered off then sublimed under vacuum at room temperature. 5.1 g (90.4% yield) of large orange crystals were obtained. Found: Co, 17.50; py, 48.65; CO, 34.04. $[py_2H][Co(CO)_4]$ calcd.: Co, 17.88; py, 47.88; CO, 33.94%.

Reaction between $Co_2(CO)_8$ and $Co(O_2CC_2H_5)_2$ in THF at P(CO) 600 and 10 mmHg, respectively. A saturated THF solution of $Co(O_2CC_2H_5)_2$ (about 10^{-2} *M*, 22° C) showed a broad band at 1600 cm^{-1} in the CO stretching region. To a suspension of 0.615 g (3 mmol) of $Co(O_2CC_2H_5)_2$ in 100 ml of THF were added 1.026 g (3 mmol) of $Co_2(CO)_8$ at 22° C (*P*(CO) 600, *P*(THF) 160 mmHg). Gas evolution was observed (91 ml, 2.97 mmol in 5 h) and a clean solution was obtained (IR spectrum in Fig. 2a). The CO atmosphere was repeatedly diluted with Ar, until a 1.3 CO percentage (*P*(CO) 10 mmHg) was determined in the gas phase in equilibrium with the solution (IR spectrum in Fig. 2b). At *P*(CO) lower than 10 mmHg, a black solid separated from the solution. When the *P*(CO) was restored to 600 mmHg, gas absorption took place and the IR spectrum of Fig. 2a was reformed.

Reaction between $Co_2(CO)_8/Co(O_2CC_2H_5)_2$ and synthesis gas in THF. A solution of dicobalt octacarbonyl (0.925 g, 2.7 mmol) and 0.550 g (2.68 mmol) of $Co(O_2CC_2H_5)_2$ in 90 ml of THF was stirred under CO/H_2 1/1 in a 2 liter flask at 22° C. Gas absorption was observed and the original CO/H_2 1/1 atmosphere, was renewed every 2 h. After 8 h the spectrum of Fig. 2c was observed, and no further change was noted. The gas composition in equilibrium with the solution was checked by gas cromatographic analysis (Found: CO, 39.52; H_2, 39.35%). By IR comparison with standard THF/C_2H_5COOH solutions, 5.15 mmol of C_2H_5COOH were shown to be present at the end of the reaction.

A solution of 0.880 g (2.57 mmol) of $Co_2(CO)_8$ and 0.530 g (2.58 mmol) of $Co(O_2CC_2H_5)_2$ in 86 ml of THF was stirred under $CO/H_2/Ar$ 1/3.3/2.3 in a 2 liter flask at 22° C. The atmosphere was renewed every 6 h. After 24 h the IR spectrum of Fig. 2d was observed and no further change was noted. The gas composition in equilibrium with the solution was checked by gas cromatographic analysis (Found: CO, 11.84; H_2, 39.47%).

Reaction between $Co_2(CO)_8$ and C_2H_5COOH in THF. Dicobalt octacarbonyl (0.437 g, 1.28 mmol) was dissolved in 30 ml of THF in a 375 ml flask, and under vacuum, through a rubber septum, were added 0.126 ml (1.69 mmol) of C_2H_5COOH. After 48 h at 22° C the flask was filled with Ar and a gas aliquot was analyzed by gas cromatography (Found: H_2, 3.3; CO, 27.2%. $CO/H_2 = 8.2$). The IR spectrum of the resulting solution shows absorptions at 2062, 2056, 1887, 1858, 1743 and 1618 cm^{-1}.

Reaction between $Co_2(CO)_8$ and $CoCl_2$ in THF. Dicobalt octacarbonyl (0.245 g, 0.72 mmol) was dissolved in 24 ml of THF under P(CO) 600 mmHg at 22° C. On addition of 0.092 g (0.71 mmol) of anhydrous $CoCl_2$, gas evolution was observed (16.6 ml, 0.54 mmol in 6 h). At this stage the IR spectrum of the solution was that shown in Fig. 3a. The atmosphere was repeatedly diluted with Ar until a 1.3 CO percentage (P(CO) 10 mmHg) was determined in gases in equilibrium with the solution (IR spectrum in Fig. 3b). When P(CO) was restored to 600 mmHg, gas absorption occurred and the IR spectrum of Fig. 3a was reformed.

Reaction between $Co_2(CO)_8/CoCl_2$/synthesis gas and 1-hexene in THF. Dicobalt octacarbonyl (0.310 g, 0.91 mmol) and $CoCl_2$ (0.120 g, 0.92 mmol) were dissolved in 30 ml of THF and the solution equilibrated under a $P(CO) = P(H_2) =$ 300 mmHg at 22° C (IR spectrum in Fig. 4a). Upon addition of 2.4 ml (19 mmol) of 1-hexene, gas absorption began. After 15 h the IR spectrum of the solution became that shown in Fig. 4b. After 48 h of reaction, 3.76 mmol of C_7 aldehydes were determined by GLC in 4/4/1 (normal/branched/internal) ratio.

Reaction between $Co_2(CO)_8$ and CoI_2 in THF. Dicobalt octacarbonyl (1.090 g, 3.19 mmol) and CoI_2 (0.990 g, 3.16 mmol) were dissolved in 107 ml of THF at 22° C. Aliquots of the solution, equilibrated under P(CO) 600, $P(CO) = P(H_2) =$ 300, or P(CO) 10mmHg, respectively, were examined by IR spectroscopy (Fig. 5a, b, c).

Dicobalt octacarbonyl (1.44 g, 4.21 mmol) and CoI_2 (3.42 g, 1.09 mmol) were dissolved in 70 ml of THF, and CO was continuously pumped off by refluxing the solution at 28° C for 24 h with a manostat (P 200 mmHg) interposed between the vacuum pump and the top of condenser. A black solid was formed and removed by filtration. The mother liquor was maintained at dry ice temperature for 10 h, and this brought about the precipitation of green leaflets (unreacted $CoI_2 \cdot n$THF) which were removed by filtration at −78° C. The resulting solution was kept in dry ice for an additional 24 h: mauve crystals, which decomposing on drying, were formed and recovered by decantation. The crystals were redissolved in 30 ml of THF, to give a solution which was dark green at room temperature but pale yellow at −78° C. The IR spectra of the solution were recorded at 240–298 K. (Fig. 6a, b, c).

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References and notes

1 F. Ungvàry, J. Organomet. Chem., 36 (1972) 363.

2 A. Sisak, F. Ungvàry, L. Markò, Organometallics, 2 (1983) 1244 and ref. therein.

3 G. Fachinetti, F. Del Cima, G. Sbrana, T. Funaioli, J. Organomet. Chem., 287 (1985) C23.

4 G. Fachinetti, G. Fochi, T. Funaioli, J. Organomet. Chem., 301 (1986) 91.

5 G. Fachinetti, G. Fochi, T. Funaioli, P.F. Zanazzi, J. Chem. Soc. Chem. Comm., (1987) 89.

6 G. Fachinetti, G. Fochi, T. Funaioli, P.F. Zanazzi, Angew. Chem. Int. Ed. Engl., 26 (1987) 680.

7 W. Hieber, W. Hüber, Z. Elektrochem., 57 (1953) 331.

8 F. Calderazzo, G. Fachinetti, F. Marchetti, P.F. Zanazzi, J. Chem. Soc. Chem. Comm., (1981) 181.

9 For other ion-pairing interactions involving $Co(CO)_4^-$ anion see: (a) W. Edgell, S. Chanjansri, J. Am. Chem. Soc., 102 (1980) 147; (b) W. Edgell, S. Hedge, A. Barbetta, ibid., 100 (1978) 1406; (c) D.P. Schussler, W.R. Robinson, W. Edgell, Inorg. Chem., 13 (1974) 153; (d) W. Edgell, J. Lyford, J. Am. Chem. Soc., 93 (1971) 6407; (e) W. Edgell, J. Lyford, A. Barbetta, C.I. Jose, ibid., 93 (1971) 6403. For ion-pairing interactions of transition metal carbonyl anions see: M.Y. Darensbourg, Prog. Inorg. Chem., 33 (1985) 221.

10 P. Chini, Chim. Ind., 42 (1960) 133.

11 P. Chini, Chim. Ind., 42 (1960) 137.

12 H.N. Adams, G. Fachinetti, J. Strähle, Angew. Chem. Int. Ed. Engl., 19 (1980) 404.

13 G. Fachinetti, J. Chem. Soc. Chem. Comm., (1979) 396.

14 M. Orchin, Acc. Chem. Res., 14 (1981) 259.

15 P. Pino, Ann. N.Y. Acad. Sci., 415 (1983) 111.

16 W. Galamb, G. Pályi, J. Chem. Soc. Chem. Comm., (1982) 487; W. Galamb, G. Pályi, E. Szerencsés, I. Orszag, F. Ratkovics, 4th ISHC Leningrad, Sept. 1984, Proc. 4 p. 51.

17 M.Y. Darensbourg, H. Barros, C. Borman, J. Am. Chem. Soc., 99 (1977) 1647.

18 J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Book, Mill Valley, California 1987; Chapter 5 and ref. therein.

19 L.D. Tenney, A.V. Logan, J. Am. Chem. Soc., 62 (1940) 1276.

20 G. Fachinetti, L. Balocchi, F. Secco, M. Venturini, Angew. Chem. Int. Ed. Engl., 20 (1981) 204.