Journal of Organometallic Chemistry, 232 (1982) 81—87
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REDUCTIVE CARBONYLATION OF PHOSPHINO-COMPLEXES OF COBALT(II), A KINETIC INVESTIGATION

M. BASATO, M. BRESSAN

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, University of Padua, 35100 Padova (Italy)

and P. RIGO

Istituto di Chimica, University of Udine, 33100 Udine (Italy)

(Received January 4th, 1982)

Summary

The stoichiometry and kinetics of the reaction of carbon monoxide with $[CoI_2(CO)(PEt_3)_2]$ were examined in different solvents and in the presence of free PEt_3. The results are interpreted in terms of a mechanism in which an iodide-bridged dicobalt species undergoes carbon monoxide addition to give an intermediate which is reduced by external PEt_3.

It is well known that salts and complexes of cobalt(II) can react with carbon monoxide by reductive carbonylation, with formation of carbonyls of the metal in low oxidation states [1]. In particular, a variety of cobalt(I) carbonyl derivatives can be easily prepared from cobalt(II) even at ambient carbon monoxide pressure. For instance, from aqueous solutions of $[Co(CN)_5]^{3-}$, the carbonyl $[Co(CN)_3(CO)_2]^{2-}$ is obtained [2], while alcoholic solutions of phosphines (P) and cobalt(II) salts containing low coordinating anions give $[Co(CO)_n(P)_{5-n}]^+$ derivatives [3]. Moreover, it has been reported [4,5] that the complexes $[CoX_2(PR_3)_n]$ ($n = 2, 3$; X = halogen or pseudohalogen) can react with carbon monoxide with formation of $[CoX_2(CO)(PR_3)_2]$ adducts. In some cases [5], depending on the nature of X and PR_3, these compounds undergo reductive carbonylation to $[CoX(CO)_2(PR_3)_2]$. Similar behaviour has been reported for the complex $[CoI(P(OEt)_2Ph)_4]^+$ [6].

The mechanism of such reactions has been little investigated and the only reported kinetic study is that by Halpern on the carbonylation of pentacyanocobaltate(II) ion [2]. We have now investigated in detail the reductive carbonylation of a series of $[CoX_2(PR_3)_n]$ complexes in different solvents with (and without) added phosphine, with the aim of establishing the stoichiometry and the mechanism of the reaction.

0022-328X/82/0000—0000/$02.75

Results and discussion

The reaction between carbon monoxide and cobalt(II) complexes of the type $[CoX_2(PR_3)_n]$ (n = 2 or 3) leads to reversible formation of the carbonyl derivatives $[CoX_2(CO)(PR_3)_2]$ (eq. 1)

$$[CoX_2(PR_3)_n] + CO \rightleftharpoons [CoX_2(CO)(PR_3)_2] + (n-2)\,PR_3 \qquad (1)$$

These can further react to give carbonyl derivatives of cobalt(I) of composition $[CoX(CO)_2(PR_3)_2]$ [5]. Preliminary investigations carried out on a series of $[CoX_2(PR_3)_n]$ complexes have shown that $[CoI_2(PEt_3)_2]$ exhibits the most favourable combination of reaction rates and ease of product characterization for a kinetic and mechanistic study of the process.

Stoichiometry and products

Differing stoichiometries were found for the reaction between carbon monoxide and $[CoI_2(PEt_3)_2]$, depending on the nature of solvent and the absence or presence of added phosphine.

In cyclohexane and 2-propanol and in the presence of excess PEt_3, the cobalt(II) derivative is quantitatively reduced to $[CoI(CO)_2(PEt_3)_2]$ according to eq. 2:

$$2[CoI_2(PEt_3)_2] + 4\,CO + PEt_3 \rightarrow 2[CoI(CO)_2(PEt_3)_2] + \text{“}PEt_3I_2\text{”} \qquad (2)$$

The above stoichiometry was confirmed as follows: (i) carbon monoxide uptake measurements indicate that 2 mol of CO per mol of cobalt(II) are absorbed; (ii) quantitative IR analyses, using standard solutions of $[CoI(CO)_2(PEt_3)_2]$ indicate that the original cobalt(II) is quantitatively converted into the cobalt(I) carbonyl; (iii) GLC analyses rule out the possibility that carbon monoxide and/or the solvent act as reducing agents in the process; (iv) ^{31}P NMR measurements show that about one mol of PEt_3 is consumed per two mol of formed $[CoI(CO)_2(PEt_3)_2]$. The species PEt_3I_2 [7] could not be detected by NMR in the reaction mixture (PEt_3I_2 is sparingly soluble in the solvents used).

In 2-propanol, but in the absence of added phosphine, the reaction of carbon monoxide with $[CoI_2(PEt_3)_2]$ results in a non-stoichiometric reduction of cobalt(II) to cobalt(I) (eq. 3):

$$5\,[CoI_2(PEt_3)_2] + 8\,CO \rightarrow 4\,[CoI(CO)_2(PEt_3)_2] + \text{“}CoI_2 \cdot 2\,PEt_3I_2\text{”} \qquad (3)$$

Gas volumetric measurements indicate that approximately 1.6 mol of CO *per* mol of cobalt(II) are consumed. Accordingly, IR analyses confirm that the amount of $[CoI(CO)_2(PEt_3)_2]$ formed is equivalent to only 80% of the starting cobalt(II). However, the visible spectra of the final solutions show that the $[CoI_2(CO)(PEt_3)_2]$ has completely disappeared and that a new cobalt(II) species (likely a four-coordinate tetrahedral one) has been formed in an approximately 20% yield. The nature of this product, formulated as “$CoI_2 \cdot 2PEt_3I_2$” in eq. 3, is still undefined and attempts to isolate the compound in the solid state gave green paramagnetic powders with erratic composition (μ_{eff} ca. 4.5 BM per cobalt atom). However, the “$CoI_2 \cdot 2PEt_3I_2$” can be easily converted into (i) the well known $[CoI_4]^{2-}$ ion by addition of excess $[Bu_4N]I$, or (ii) the starting

[$CoI_2(PEt_3)_2$] complex by treatment with phosphine in the absence of carbon monoxide.

In cyclohexane under ambient conditions the reduction in the absence of added phosphine is very slow. Experiments at higher pressure (ca. 10 atm) show a reaction pattern in agreement with eq. 3.

In some other solvents, such as 1,2-dichloroethane and benzene, the reaction qualitatively also proceeds according to eq. 3, i.e. with only partial reduction of the cobalt(II) and formation of the green product "$CoI_2 \cdot 2PEt_3I_2$", but in these solvents the usual rapid absorption of 1 mol of CO per mol of [$CoI_2(PEt_3)_2$] is followed by a very slow absorption of only 0.1—0.2 additional mol of CO, (instead of 0.6 as in the previous cases) with a corresponding conversion of only 50—60% of the starting cobalt(II) into [$CoI(CO)_2(PEt_3)_2$] (instead of 80%).

For the other [$CoI_2(PR_3)_2$] complexes investigated (PR_3 = PPh_3, PPh_2Et, $PPhEt_2$, PPh_2Me) the evidence is qualitatively in agreement with eq. 3. For the tris-phosphino [$CoI_2(PPhMe_2)_3$] derivative, which liberates phosphine in the first carbonylation step (eq. 1), almost quantitative conversion to [$CoI(CO)_2(PPhMe_2)_2$] is observed, according to eq. 2.

Reactivity

The most detailed and extensive kinetic measurements were made on the complex [$CoI_2(PEt_3)_2$] in cyclohexane solution in the presence of added PEt_3.

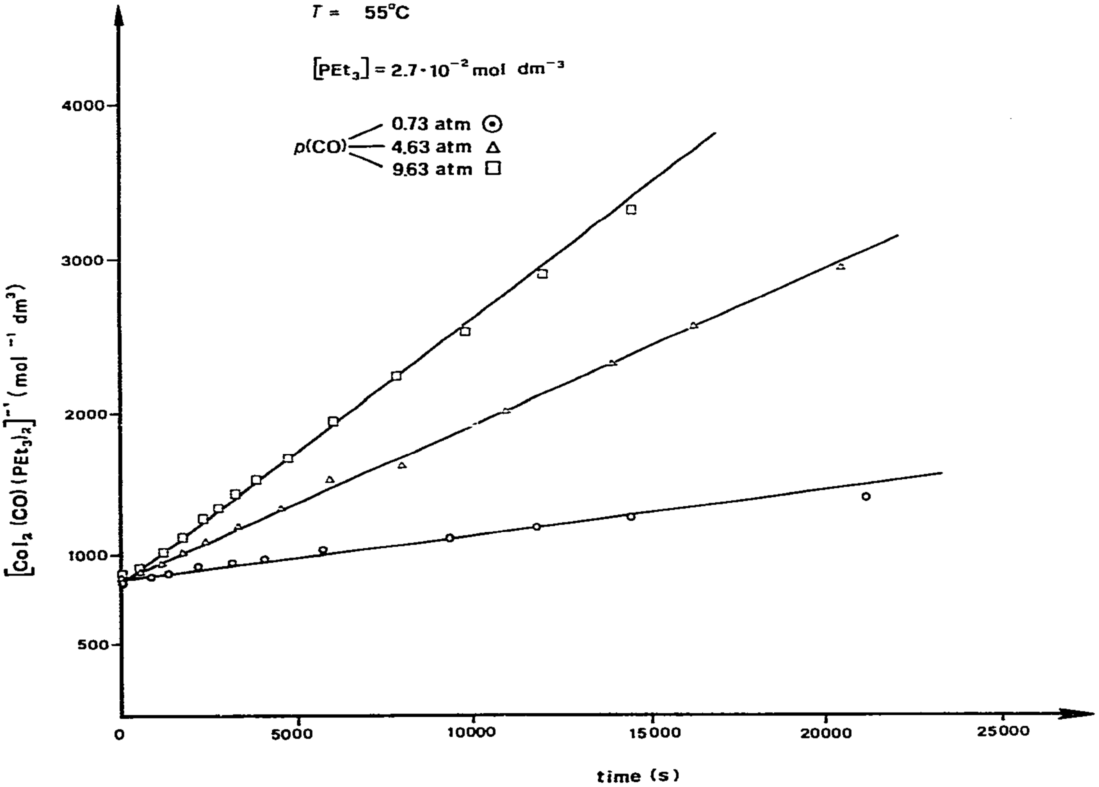

Fig. 1. Representative pseudo-second-order rate plots at various carbon monoxide pressures.

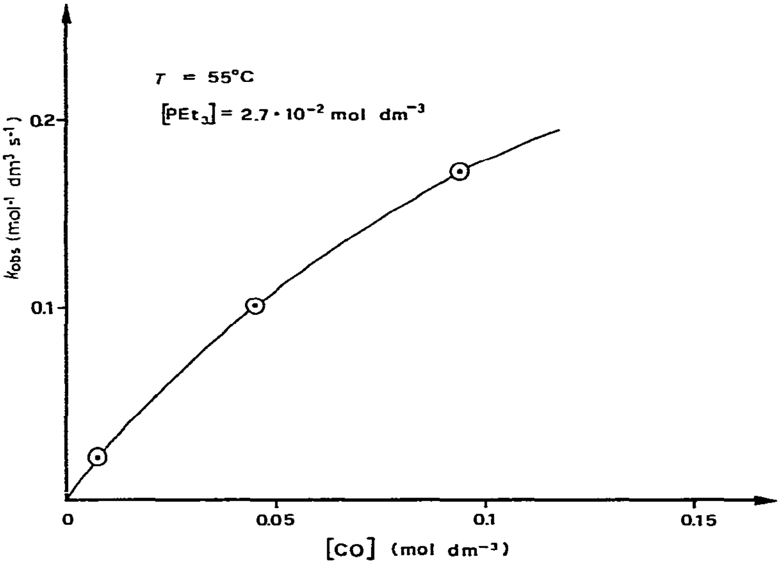

Fig. 2. Dependence of k_{obs} on carbon monoxide concentration.

Addition of excess PEt_3 to the solutions markedly increases the rate and simplifies the spectral changes, which indicate, in this case, the occurrence of a single step following the fast addition of carbon monoxide to $[CoI_2(PEt_3)_2]$. Accordingly, the rate of gas uptake parallels the rate of successive formation of $[CoI_2(CO)(PEt_3)_2]$ and $[CoI(CO)_2(PEt_3)_2]$, thus ruling out appreciable accumulation of other intermediates.

Two series of kinetics at 55°C and $[Co^{II}]_0 = 1.2 \times 10^{-3}$ M have been performed: the first at three different CO pressures (0.73, 4.63 and 9.63 atm) and $[PEt_3] = 2.7 \times 10^{-2}$ M, and the second at constant p(CO) 9.63 atm and various $[PEt_3]$ (1.1×10^{-2}, 2.7×10^{-2}, 5.4×10^{-2}, and 10.8×10^{-2} M). Under these experimental conditions (constant p(CO) and $[PEt_3]$ in the single runs) the kinetics were pseudo-second order in the concentration of the complex corresponding to the integrated rate law $[CoI_2(CO)(PEt_3)_2]_T{}^{-1}$ — $[CoI_2(CO)(PEt_3)_2]_0{}^{-1} = k_{obs.} \cdot T$. Figure 1 shows the good linearity obtained by plotting $[CoI_2(CO)(PEt_3)_2]_T{}^{-1}$ vs. time, the actual concentration values of $[CoI_2(CO)(PEt_3)_2]$ being calculated from the difference between the initial value (= weighted concentrations of $[CoI_2(PEt_3)_2]$) and those of $[CoI(CO)_2(PEt_3)_2]$, determined by quantitative analysis of the IR spectrum at various times. The $k_{obs.}$ values determined from the slopes of these plots increase with [CO] and $[PEt_3]$, as shown in Fig. 2 and 3 respectively, defining an empirical rate law of the type $k_{obs.} = 0.35\,[CO][PEt_3]/(2.6 \times 10^{-3} + [CO][PEt_3])$, where 0.35 is the limiting $k_{obs.}$ value at higher CO and PEt_3 concentrations. The kinetic behaviour of reaction 2 can be represented by the rate law (4):

$$-\frac{d[CoI_2(CO)(PEt_3)_2]}{dt} = \frac{d[CoI(CO)_2(PEt_3)_2]}{dt} = \frac{0.35[CO][PEt_3][CoI_2(CO)(PEt_3)_2]^2}{2.6 \times 10^{-3} + [CO][PEt_3]} \qquad (4)$$

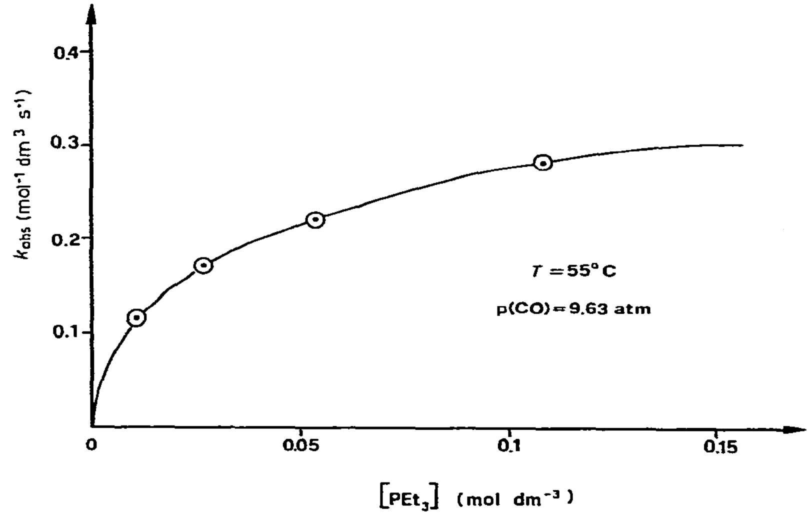

Fig. 3. Dependence of k_{obs} on PEt$_3$ concentration.

The rate exhibits a small temperature dependence, as indicated by a run performed at 40°C.

The reductive carbonylation of $[CoI_2(PEt_3)_2]$ in 2-propanol at ambient conditions and in the presence of added phosphine appears to be definitely faster. For example, for $[CoI_2(PEt_3)_2] = 1.2 \times 10^{-3}$ M and a 50 fold PEt$_3$ excess, the absorption of carbon monoxide appears to be almost complete in less than 1 min. In the same solvent, but in the absence of added phosphine, the conversion of the cobalt(II) derivative into $[CoI(CO)_2(PEt_3)_2]$ proceeds in a complex manner. In all examined cases, a first fairly rapid step (20—30 min. at 20°C and 1.1 atm CO pressure), in which about 30% of the starting cobalt(II) is reduced to cobalt(I), is followed by a second rather irreproducible step.

The salts $[Bu_4N]ClO_4$ and $[Bu_4N]I$ ($5 \times 10^{-2}M$) have similar rate-increasing effects, indicating the absence of any specific inhibition by iodide ions.

As stated above, the reduction does not proceed in cyclohexane at room conditions in the absence of added PEt$_3$, and indications of reaction were observed, after a variable induction period, only at higher CO pressures (10 atm).

Semiquantitative kinetic measurements on the reactivity of various $[CoX_2(CO)(PR_3)_2]$ complexes ($X = I$; $PR_3 = PMe_2Ph$, $PMePh_2$; $X = Br$; $PR_3 = PMe_2Ph$) confirm that the rate of the reductive carbonylation markedly depends on the nature of X ($I > Br$) and PR$_3$ ($PMe_2Ph > PEt_3 > PMePh_2$).

The available kinetic information does not discriminate between several alternative mechanisms. A mechanism for the reductive carbonylation in cyclohexane which appears to be plausible on chemical grounds is depicted in the following scheme.

$$[CoI_2(PEt_3)_2] + CO \overset{\text{fast}}{\rightleftarrows} \underset{(A)}{[CoI_2(CO)(PEt_3)_2]}$$

$$2[CoI_2(CO)(PEt_3)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(A\text{-}A)}{[CoI_2(CO)(PEt_3)_2]_2}$$

$$[CoI_2(CO)(PEt_3)_2]_2 + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(B)}{[(PEt_3)_2(CO)_2ICo{-}I{-}CoI_2(CO)(PEt_3)_2]}$$

$$[(PEt_3)_2(CO)_2ICo{-}I{-}CoI_2(CO)(PEt_3)_2] + PEt_3 \xrightarrow{k_3}$$
$$[CoI(CO)_2(PEt_3)_2] + [CoI(CO)(PEt_3)_2] + \text{“}PEt_3I_2\text{”}$$

$$[CoI(CO)(PEt_3)_2] + CO \xrightarrow{\text{fast}} [CoI(CO)_2(PEt_3)_2]$$

The proposed mechanism implies a fast preequilibrium step with quantitative formation of the five-coordinate carbonyl adduct of cobalt(II) (A), which dimerizes via an iodide bridged dicobalt complex (A-A). This dinuclear species can undergo CO addition at one of the two cobalt atoms to give an intermediate (B) which is reduced by PEt_3 to the cobalt(I) carbonyl. Assuming that A-A and B are very reactive intermediates, rate equation 5 is obtained:

$$-\frac{d[CoI_2(CO)(PEt_3)_2]}{dt} = \frac{d[CoI(CO)_2(PEt_3)_2]}{dt}$$
$$= \frac{2\,k_1k_2k_3[CO][PEt_3][CoI_2(CO)(PEt_3)_2]^2}{k_{-1}k_{-2} + k_{-1}k_3[PEt_3] + k_2k_3[CO][PEt_3]} \tag{5}$$

Our experimental data applied to eq. 5 give $k_1 = 0.18\,M^{-1}\,s^{-1}$ and $k_{-1}k_{-2}/k_2k_3 = 2.6 \times 10^{-3}\,M^2$ and also indicate that in our experimental conditions, i.e. $[PEt_3] = (1.1\text{—}10.8) \times 10^{-2}\,M$ and $p(CO)$ 0.73—9.63 atm, the term $k_{-1}k_3[PEt_3]$ is significantly smaller than $k_{-1}k_{-2} + k_2k_3[CO][PEt_3]$.

The formation of iodide-bridged dicobalt complexes in the course of the reductive process is in agreement with the observation that the overall rate of the reaction for the $[CoX_2(CO)(PR_3)_2]$ complexes follows the order I > Br ≃ Cl [5]. The main feature of this mechanism is the fundamental role played by PEt_3 in the reductive step. It seems likely that the electron transfer implies a phosphine attack at an iodide ligand rather than to a coordinatively saturated cobalt atom. One cannot rule out the possibility that the reaction between B and PEt_3 is also itself a composite process, in which a preliminar dismutation of B to cobalt(I) and cobalt(III) occurs. Indeed, a dismutative mechanism has been already proved for the reaction of $[Co(CN)_5]^{3-}$ with CO, which gives equimolar amounts of $[Co(CN)_3(CO)_2]^{2-}$ and $[Co(CN)_6]^{3-}$ [2]. Dismutation of cobalt(II) complexes to cobalt(I) and cobalt(III) has been also observed when cobalt(II) salts react with difluorophenylphosphine [8] or some phosphites [9].

The proposed mechanism for the reductive carbonylation of $[CoI_2(PEt_3)_2]$ is also consistent with the observed behaviour in the absence of added phosphine, both in 2-propanol at ambient $p(CO)$ and in cyclohexane at higher (ca. 10 atm) $p(CO)$. It seems likely that in these cases small amounts of PEt_3 (which is involved in the redox step) can be released in solution, because of some solvolysis in the polar solvent 2-propanol or of some dissociation and/or decomposition in cyclohexane of the starting cobalt(II) complex.

A final comment concerns the influence of the nature of the phosphine on the reduction process. It was observed previously that $[CoI_2(PCy_3)_2]$ and $[CoI_2(PPh_3)]$ react very slowly with CO under comparable experimental conditions [5]. This fact and the reported reactivity sequence $PMe_2Ph > PEt_3 > PMePh_2$ suggest that steric hindrance by the phosphorus ligand has a marked inhibiting effect on the reductive carbonylation reaction.

Experimental

Materials. Phosphines and cobalt complexes were prepared by standard methods. $[Bu_4N]ClO_4$, $[Bu_4N]I$, and NaI were commercial high purity products; $NaClO_4$ was obtained from the hydrated salt by two-days heating under vacuum at 120°C. Solvents were purified by standard methods and kept on the dark. Carbon monoxide was an high purity SIO product.

Stoichiometry determination. The nature and relative quantity of cobalt complexes were generally determined by IR or visible-UV spectroscopy as described. The volume of CO consumed at constant pressure was measured in a standard thermostatted gas-buret apparatus. In addition, the composition of the reacting solutions was checked by conductometric and GLC analyses.

Kinetic measurements. The reaction rate was studied at atomospheric or higher ($\leqslant 10$ atm) CO pressure, depending on the type of complex, solvent, and concentration of phosphine. In all cases the solvent (10 or 25 cm^3) after careful deoxygenation by freeze-pump-thaw cycles, was transferred under CO to a Schlenk tube containing known amounts of the solid complex. This transfer was made through stainless-steel tubing, inserted through Suba-seal rubber stoppers. After dissolution of the complex and eventual addition of the appropriate phosphine from a microsyringe, the resulting solution was either kept in the tube or transferred, through a similar tubing system, to a small stainless steel pressure bottle (100 cm^3) for reactions at higher pressures. In both cases the reaction vessel was immersed in an oil-bath thermostatted to ± 0.2°C and aliquots were removed periodically from the Schlenk tube through the usual tubing or from the bottom of the autoclave through a microvalve connected. In this last case the first fraction (ca. 1 cm^3) of each portion was always discarded. Samples were ejected directly into an IR cell and the spectra scanned immediately in the ν(CO) region. The reaction was most conveniently followed by monitoring the bands in the 2000—1850 cm^{-1} region due to $[CoX_2(CO)(P)_2]$ and $[CoX(CO)_2(P)_2]$. Carbon monoxide concentrations were computed from the measured partial pressures using literature solubility data [10].

Instruments. IR and visible-UV spectra were monitored with a Perkin—Elmer 457 and Optica CF4R spectrophotometers, respectively. Conducibility measurements were performed with a Radiometer CDM-3 bridge and GLC analyses with an Hewlett—Packard 5750 instrument.

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