

# Neutral Cobalt Carbonyl Catalysts for the Equilibration between CO and P(OPh)<sub>3</sub> Ligands in Carbonylcobaltates

Ennio Ciuffarin, Giuseppe Fachinetti,\* Tiziana Funaioli and Mauro Isola

**Abstract:** The substitution reaction of  $[\text{Co}(\text{CO})_4]^-$  by  $\text{P}(\text{OPh})_3$  was investigated in THF. Under a CO atmosphere, the reaction consists of an equilibrium, which, in order to be established, needs  $[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$ . The catalysis by this neutral carbonyl is formally related to

a previously reported case, where either  $[\text{Co}_2(\text{CO})_8]$  or  $[\text{Co}_4(\text{CO})_{12}]$  was found to

## Keywords

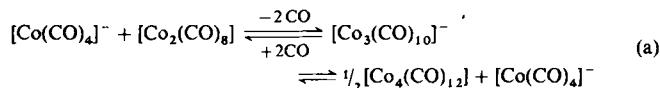
carbonyl complexes · cobalt compounds · kinetics · mechanistic studies

be necessary for the  $^{13}\text{CO}$  scrambling in  $[\text{Co}(\text{CO})_4]^-$ . The kinetic analysis reported in this paper indicates, however, that the two CO labilizations differ in their mechanism—the substitution by  $\text{P}(\text{OPh})_3$  is ascribed to a disproportionation–synproportionation of  $[\text{Co}_2(\text{CO})_6(\text{P}(\text{OPh})_3)_2]$ .

## Introduction

Salts of  $[\text{Co}(\text{CO})_4]^-$  are important organometallic reagents extensively used in both synthetic<sup>[11]</sup> and catalytic<sup>[22]</sup> reactions. Fundamental studies of this carbonyl anion have included investigations into its electrochemistry,<sup>[3]</sup> nucleophilicity,<sup>[4]</sup> and hetero-<sup>[5]</sup> and homonuclear<sup>[6]</sup> ion pairing. It was shown that ion pairing with polarizing counterions in ethereal solvents makes the CO ligands of  $[\text{Co}(\text{CO})_4]^-$  exceptionally labile<sup>[7]</sup> with respect to other mononuclear, homoleptic 18-electron carbonyl-metallocates.<sup>[8]</sup> Such a labilizing effect was manifested in  $^{13}\text{CO}$  scrambling<sup>[7a]</sup> as well as in CO substitution reactions by phosphites, phosphines and activated olefins,<sup>[7b]</sup> and was explained with the assistance of tight ion pairs in promoting a dissociative mechanism. Accordingly, the 16-electron species  $[\text{Co}(\text{CO})_3]^-$  was proposed as an intermediate. However, we envisaged a less straightforward reaction pathway for  $^{13}\text{CO}$  scrambling: we realized, in fact, that  $\text{Na}[\text{Co}(\text{CO})_4]$  fails to incorporate  $^{13}\text{CO}$  in THF solution, in spite of apparent formation of tight ion pairs, when care is taken to avoid any contamination by neutral cobalt carbonyls.<sup>[9]</sup> On the other hand, unperturbed  $[\text{Co}(\text{CO})_4]^-$  with the nonpolarizing  $\text{PPN}^+$  counterion ( $\text{PPN}^+ = \text{bis}(\text{triphenylphosphoranylidene})\text{ammonium}$ ) exchanges with  $^{13}\text{CO}$  when  $[\text{Co}_2(\text{CO})_8]$  has been added: catalytic amounts of neutral cobalt carbonyl rather than ion pairing allow the  $^{13}\text{CO}$  scrambling reactions of  $[\text{Co}(\text{CO})_4]^-$ .<sup>[9]</sup> The role of the ion pairing is then limited to the in situ generation of  $[\text{Co}_2(\text{CO})_8]$ : the  $^{13}\text{CO}$  scrambling reactions follow a chemical oxidation, and only when perturbed by a polarizing counterion does  $[\text{Co}(\text{CO})_4]^-$  react with traces of adventitious oxygen to give the  $[\text{Co}_2(\text{CO})_8]$  catalyst.<sup>[10]</sup> On these grounds, in place of a dissociative mechanism we pro-

posed the fast Equilibrium (a), direct evidence for which was obtained in ethereal solutions where neutral and anionic cobalt



carbonyls are in the same concentration range.<sup>[11]</sup> In accord with such a mechanism, based on a redox condensation equilibrium, it was shown that, under an inert atmosphere,  $[\text{Co}_4(\text{CO})_{12}]$  is a catalyst for ligand exchange between  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{Co}^{13}\text{CO}]^-$ , and that  $[\text{Co}(\text{CO})_4]^-$ , in turn, catalyses the  $^{13}\text{CO}$  scrambling reactions of neutral cobalt carbonyls.<sup>[9]</sup>

On these grounds, we can conclude that the thermal dissociation of CO ligand from  $[\text{Co}(\text{CO})_4]^-$  constitutes a high-energy process even in the presence of ion pairing and that it therefore cannot even be invoked in  $[\text{Co}(\text{CO})_4]^-$  substitution reactions by phosphites, phosphines and activated olefins. On the other hand, a redox condensation mechanism of the type shown in Equation (a) also seems unlikely for the latter reactions, which proceed at a much slower rate with respect to the CO scrambling. Furthermore, redox condensation equilibria among substituted neutral and anionic cobalt carbonyls have never been observed. In order to better understand these synthetically useful substitution reactions, we investigated the chemistry of  $[\text{Co}(\text{CO})_4]^-$  in the presence of CO and  $\text{P}(\text{OPh})_3$  as competing ligands in tetrahydrofuran (THF) solution.

## Results and Discussion

Like the CO scrambling,<sup>[9]</sup> the substitution reaction of  $[\text{Co}(\text{CO})_4]^-$  by  $\text{P}(\text{OPh})_3$  required the presence of neutral cobalt carbonyls. When care was taken to avoid any contamination by adventitious oxidants of the anionic carbonyl, no substitution products were formed in THF solutions of  $\text{Na}[\text{Co}(\text{CO})_4]$ <sup>[12]</sup> or

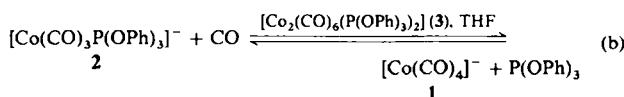
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PPN[Co(CO)<sub>4</sub>] (PPN<sup>+</sup>-1) containing an excess of P(OPh)<sub>3</sub>. On the other hand, CO substitution by P(OPh)<sub>3</sub> was initiated by adding catalytic amounts of [Co<sub>2</sub>(CO)<sub>8</sub>], and we attempted to subject this catalytic effect to kinetic analysis. Kinetic runs were carried out at constant concentrations of exchanging ligands, that is, by keeping the  $P_{CO}$  constant and by employing a large excess of phosphite. Under these conditions, however, PPN<sup>+</sup>-1 and PPN[Co(CO)<sub>3</sub>P(OPh)<sub>3</sub>] (PPN<sup>+</sup>-2) were found to be in equilibrium [Eq. (b)]. Moreover, the actual catalyst for the reaction was [Co<sub>2</sub>(CO)<sub>6</sub>(P(OPh)<sub>3</sub>)<sub>2</sub>] (3), rather than [Co<sub>2</sub>(CO)<sub>8</sub>] itself. In fact, the latter was rapidly and quantitatively converted into 3 by P(OPh)<sub>3</sub>, both under CO or an inert atmosphere; the reaction is fast on the timescale of the CO/P(OPh)<sub>3</sub> scrambling in [Co(CO)<sub>4</sub>]<sup>-</sup>. The catalytic activity of 3 was separately confirmed: 1) it promoted quantitative formation of 2 upon continuous removal of CO from a THF solution of 1 containing an excess of P(OPh)<sub>3</sub>, and 2) under a CO atmosphere, 3 brought about gas absorption by 2, which is converted back to 1 [Eq. (b)]. On the basis of these findings, the substitution reaction actually consists Equilibrium (b) catalysed by 3, where CO and P(OPh)<sub>3</sub> compete for the coordination sphere of the carbonylcobaltates. The molar ratio for the 2/1 equilibrium was determined by gas volumetric measurements or independently by quantitative IR determinations of the anionic carbonyl concentrations in the equilibrium mixture. Both techniques substantially agreed in giving a value of 0.29 for [P(OPh)<sub>3</sub>] = 0.38 M,  $P_{CO}$  = 540 Torr ([CO] = 8.3 × 10<sup>-3</sup> M)<sup>[1,3]</sup> and  $T$  = 30 °C. In spite of the large excess of phosphite with respect to CO, Equilibrium (b) lies to the right, and so we chose to carry out the kinetic runs with 2 rather than 1 as the substrate. The reaction was monitored by gas volumetric measurements.

The kinetic runs followed first-order behaviour when the concentration of the exchanging ligands (CO and phosphite) in the solution was kept constant. However, the first-order rate constant ( $k_{obs}$ ) was not independent of the initial concentration of 2 and 3. The most relevant kinetic features of this system can be summarized as follows:

- The kinetic runs follow first-order behaviour.
- The substrate 2 alone does not exchange its ligands. Only in the presence of the catalyst, can the formation of the product 1 be observed [Eq. (b)].



- The observed rate constant decreases at increasing initial concentration of 2. The data are reported in Table 1 and shown in Figure 1.

Table 1. Observed pseudo first-order rate constants for the CO/P(OPh)<sub>3</sub> scrambling [a].

$c(2)/\text{mM}$	$c(3)/\text{mM}$	$k_{obs}/\times 10^{-3} \text{ s}^{-1}$	$c(2)/\text{mM}$	$c(3)/\text{mM}$	$k_{obs}/\times 10^{-3} \text{ s}^{-1}$
25.3	0.0	0.000	25.3	4.79	6.93
25.3	0.208	2.48	6.15	1.03	5.78
25.3	0.378	2.57	10.0	1.03	4.44
25.3	0.675	4.53	19.8	1.03	3.65
25.3	1.33	5.55	30.3	1.03	3.15
25.3	2.78	6.08	39.8	1.03	2.98
25.3	3.67	6.70	72.7	1.03	2.10

[a] In all runs  $P_{CO}$  = 540 Torr ([CO] = 8.3 × 10<sup>-3</sup> M); [phosphite] = 0.38 M;  $T$  = 30 °C; solvent = THF.

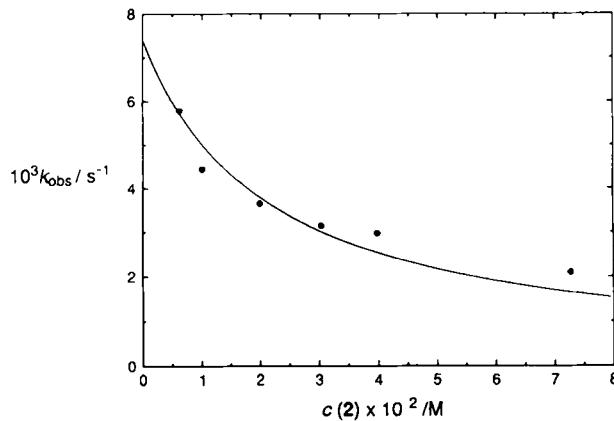


Fig. 1. Effect of the concentration of PPN[Co(CO)<sub>3</sub>P(OPh)<sub>3</sub>] (PPN<sup>+</sup>-2) on  $k_{obs}$ .

- The observed rate constant increases at increasing initial concentration of catalyst, but tends to level off. The data are reported in Table 1 and shown in Figure 2.
- The rate becomes independent of the concentration of catalyst at a concentration which is lower than the substrate's concentration.
- The rate increases with the CO pressure (Table 2).

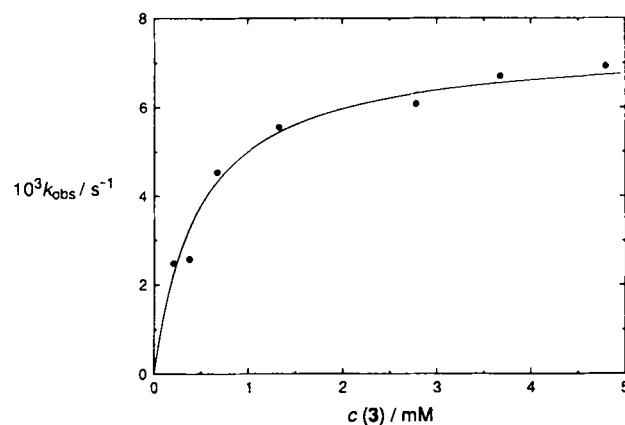


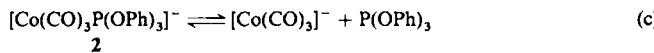
Fig. 2. Effect of the concentration of [Co<sub>2</sub>(CO)<sub>6</sub>(P(OPh)<sub>3</sub>)<sub>2</sub>] (3) on  $k_{obs}$ .

Table 2. Effect of  $P_{CO}$  on  $k_{obs}$  [a].

$P_{CO}/\text{Torr}$	300	530	720	840
$k_{obs}/\times 10^{-3} \text{ s}^{-1}$	1.87	3.05	4.18	4.50

[a]  $c(2) = 2.53 \times 10^{-2}$  M;  $c(3) = 5 \times 10^{-4}$  M;  $T$  = 30 °C.

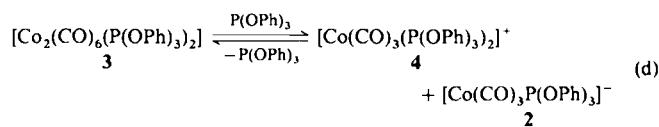
The effect of carbon monoxide on the reaction is consistent with all mechanisms where CO incorporation occurs at or before the rate determining step. The other kinetic features outlined above, on the other hand, allow one to exclude quite a number of mechanisms. Since  $k_{obs}$  decreases at increasing concentration of 2, we can exclude all mechanisms that assume a direct reaction (catalysed or not) of the negative ion with carbon monoxide. At the same time and for the same reasons, a catalysed predissociation of the substrate [Eq. (c)] followed by reaction with CO can also be excluded.



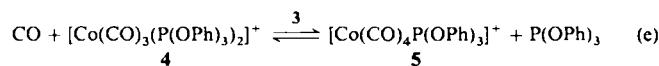
Since the reaction of the substrate to yield **1** follows first-order kinetics, the negative dependence of  $k_{obs}$  on the initial concentration of the substrate is quite peculiar; in general when a reagent forms or disappears according to a first-order rate law, the observed rate constant is independent of its initial concentration (first-order reversible or pseudo first-order reactions). Only for reactions that are at equilibrium or near equilibrium, for relaxation kinetics<sup>[14]</sup> or for isotope exchange reactions<sup>[15]</sup> can both first-order kinetics and dependence of the observed rate constant on the reagents' concentration be observed.

The data also exclude all mechanisms that assume an interaction of the catalyst with CO followed by reaction of an intermediate with the substrate, since they require a positive dependence of the rate on both catalyst and substrate concentration. CO absorption by the substrate must occur indirectly. On the other hand, the experimental fact that the rate of reaction reaches a plateau at a catalyst concentration lower than the concentration of the substrate and the negative dependence on the substrate concentration require the formation of an intermediate whose concentration depends on the rates of two competing steps.

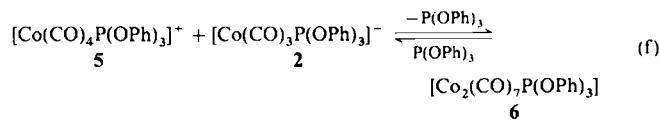
Since it has been reported that P donor ligands promote the disproportionation of neutral cobalt carbonyls to  $\text{Co}^{\text{l}}/\text{Co}^{-1}$ ,<sup>[16]</sup> we suggest that equilibria of this type constitute the root of the mechanism. In this hypothesis, Equilibrium (d) is largely dis-



placed to the left, since the cation **4** could not be spectroscopically detected in solution during the kinetic runs. Its concentration depends on the concentrations of substrate and catalyst; thus, it seems reasonable to suggest that this species is important in determining the rate of reaction. On the other hand, preliminary investigations confirmed the lability of cationic  $\text{Co}^{\text{l}}$  species when in presence of neutral cobalt carbonyls.<sup>[17]</sup> We can thus suggest Equilibrium (e). In the same hypothesis of the dispro-



portionation promoted by P donor ligands, the newly formed cation **5** is in equilibrium with the substrate **2** and with the neutral cobalt carbonyl **6** [Eq. (f)]. Even though the global equilibrium of the combined Equations (d), (e) and (f) is largely



displaced to the left under the experimental conditions, it represents the ligand exchange in the neutral cobalt carbonyl complexes, **3**  $\rightleftharpoons$  **6**. The computer simulation of this system<sup>[18]</sup> shows that  $k_{obs}$  decreases with increasing concentration of **2** and reaches a plateau at a catalyst concentration lower than the concentration of substrate, when the appropriate set of rate constants are fed into the program. Thus, the kinetic characteristics of this mechanism are identical to those found experimentally.

In order to provide a pathway for the substrate to exchange its ligands (**2**  $\rightleftharpoons$  **1**), we must also consider the disproportionation

Equilibrium (g), in addition to Equilibria (e) and (f). The com-



bination of Equilibria (e), (f), and (g) was also subjected to numerical integration. Again the simulated kinetics followed first-order behaviour, and the rate depended on the initial concentration of the reagents, showing a negative dependence on substrate concentration and dependence on the concentration of the catalyst that was initially positive and then levelled off. These equations represent the substrate's ligand exchange reaction, **2**  $\rightleftharpoons$  **1**, catalysed by the neutral cobalt complex **3** in the presence of a small amount of the neutral cobalt carbonyl **6**.

Of course, in both reactions ligand exchange of the catalyst and of the substrate must occur simultaneously. We also tried to solve the system of the combined Equations (d)–(g) by numerical integration. It was easy to find sets of parameters for this system that yielded first-order kinetics, negative dependence on the concentration of substrate and positive dependence on the concentration of catalyst. In order to be able to simulate the levelling off of the rate at increasing concentration of catalyst, we tried to feed values of rate constants into the program necessary to force a competition between two reaction steps of the mechanism. In these cases the integrations proceeded through erratic values (positive and negative) of the positive ion concentrations. However, it is known that the Runge–Kutta method (see Experimental Procedure) may not be adequate in cases of fast, opposing reactions that compensate each other nearly exactly.<sup>[18]</sup> For the time being we have no data on the mechanism of the catalysed exchange of the positive ions so that we refrain from making any comment. We would, however, like to mention that it is possible to suggest exchange reactions for the positive ions that fall in the same framework of disproportionation equilibria. Equation (e) could thus be a simplification of a more complex mechanism.

## Conclusions

A fundamental aspect in cobalt carbonyl chemistry seems to be that charged and neutral species mutually enhance the labilities of their respective CO ligands. As a matter of fact, this effect should almost always be taken into account when dealing with neutral carbonyls from which charged complexes are generated with a variety of P, N, or O donor ligands; this is also true for anionic carbonyls, which are often converted to neutral complexes by oxidants. For the latter case, this effect was hitherto unrecognized and has been documented here for the first time on the basis of kinetic measurements. The substitution by  $\text{P(OPh})_3$  in  $\text{[Co}(\text{CO})_4]^-$ , actually an equilibrium reaction where CO and phosphite compete for the coordination spheres of carbonylcobaltates, was formerly attributed to the CO ligand dissociation assisted by ion pairing. The only role of ion pairing is actually that of promoting the carbonylmetalate oxidation by adventitiously present oxidants. We have established that the product of the oxidation, that is, neutral carbonyls, are responsible for the ligand labilization in carbonylmetalates, both in  $^{13}\text{CO}$  scrambling<sup>[9]</sup> and in CO/P(OPh)<sub>3</sub> competition. We therefore consider the seemingly most obvious explanation for a substitution reaction initiated by oxidizing agents, namely, a radical chain reaction promoted by electron transfer, to be very unlikely.<sup>[19]</sup> While evidence for a redox condensation pathway in the  $^{13}\text{CO}$  scrambling was initially gathered,<sup>[9]</sup> kinetic analysis of the

CO/P(OPh)<sub>3</sub> competition indicates a mechanism based on the ligand-promoted disproportionation of **3**. Some details of the mechanism may have still not been found. They might perhaps be uncovered by a study of the catalysed exchange in the cations **4** and **5**.

## Experimental

**General Methods:** Unless otherwise stated, all manipulations were carried out under prepurified argon by standard Schlenk techniques. CO (<0.1% H<sub>2</sub>) was purchased from Matheson. [Co<sub>2</sub>(CO)<sub>8</sub>] was purchased from Strem Chemicals and sublimed (38 °C, 0.1 Torr). P(OPh)<sub>3</sub> (Aldrich-Chemie) was distilled under reduced pressure. THF (Carlo Erba) was distilled from a LiAlH<sub>4</sub> solution. Liquid samples for infrared spectra were taken with a syringe and transferred to a 0.1 mm CaF<sub>2</sub> cell. The IR spectra were recorded on a Perkin-Elmer Model FT-IR 1725-X instrument. PPN[Co(CO)<sub>4</sub>] (PPN<sup>+</sup>·**1**) [20], Na[Co(CO)<sub>4</sub>] [21], Na[Co(CO)<sub>4</sub>P(OPh)<sub>3</sub>] [22] and [Co<sub>2</sub>(CO)<sub>8</sub>P(OPh)<sub>3</sub>]<sub>2</sub> (**3**) [23] were prepared as previously described. Complex **3** was recrystallized from refluxing THF. PPN[Co(CO)<sub>3</sub>P(OPh)<sub>3</sub>] (PPN<sup>+</sup>·**2**) was prepared by metathesis of the sodium salt with PPNCl in CH<sub>3</sub>OH/H<sub>2</sub>O. Crude **2** was recrystallized twice from THF/Et<sub>2</sub>O in order to remove contaminating traces of **3**.

**Kinetic and Equilibrium Measurements:** The apparatus and procedures for the gas volumetric measurements was that described in the literature [24]. In a typical kinetic run, a 15 mL aliquot of a 0.382 M THF solution of P(OPh)<sub>3</sub> was introduced in the reaction flask, which already contained the appropriate amounts of the solid catalyst **3** and substrate **2** (the latter sealed in thin-walled vial). The flask was then connected to the burette, maintained at 30 °C and carefully saturated with CO. After the attainment of equilibrium conditions, the vial was crushed to start the run. The complete dissolution of solid **2** occurred within 30 s. The observed rate constants were obtained either from a graphical procedure or from a nonlinear least-squares fit of the experimental data to a first-order rate law. The two procedures agree within 3%.

**Computer Simulation:** Simulations of complex kinetic mechanisms were carried out on a 486 PC using the authors' version of subroutines of a nonlinear least-squares program, kindly supplied by R. Ambrosetti [18]. These subroutines use the Runge-Kutta procedure for the numerical integration of systems of differential equations describing the time evolution of the concentration terms of kinetic schemes.

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