

## Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part V.<sup>1</sup> A Kinetic Study of the Reaction of Diphenylacetylene with Hexacarbonylbis(tri-*n*-butylphosphine)dicobalt

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The kinetics of reaction of diphenylacetylene with hexacarbonylbis(tri-*n*-butylphosphine)dicobalt in decalin at 100 °C have been studied. The reaction proceeds in two stages, the initial product being the acetylene-bridged complex  $[(OC)_3Co(\mu-C_2Ph_2)Co(CO)_2PBu_3]$ . This then undergoes a substitution reaction with tributylphosphine, released in the first stage, to form  $(\mu-C_2Ph_2)\{Co(CO)_3PBu_3\}_2$ . The first stage proceeds by two main paths, one of which rises to a limiting rate with increasing  $[C_2Ph_2]$ , the other being first order in  $[C_2Ph_2]$ . Both paths are retarded by carbon monoxide and by tributylphosphine but quantitative study of the latter effect is made difficult by the occurrence of direct attack by phosphine on the complex, apparently to form a more highly substituted cobalt carbonyl. Nevertheless, it can be concluded that the two paths are probably distinguished by whether the acetylene attacks a reactive intermediate before or after reversible dissociation of both a phosphine and a carbon monoxide ligand. When dissociation occurs before attack by acetylene it appears that carbon-monoxide dissociation followed by phosphine dissociation occurs at least ten times more frequently than the reverse order. The reactive intermediate involved when attack by the acetylene occurs before dissociation can be formulated as a carbonyl-bridged complex, formed by metal migration, and the sequence of dissociation is again predominantly CO followed by phosphine.

THE kinetics of reaction of acetylenes with dicobalt octacarbonyl in toluene to form the acetylene-bridged

<sup>1</sup> Part IV, Marino Basato and Anthony Poë, *J.C.S. Dalton*, 1974, 456.

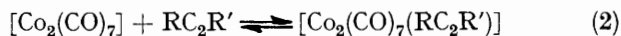
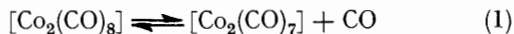
<sup>2</sup> M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *J. Amer. Chem. Soc.*, 1958, **80**, 4265; *J. Org. Chem.*, 1960, **25**, 687.

complex  $(\mu-RC_2R')\{Co(CO)_3\}_2$  have been studied by Tirpak *et al.*<sup>2</sup> and, more recently, by Ellgen<sup>3</sup> and by Ungváry and Markó.<sup>4</sup> In all cases rates of reaction

<sup>3</sup> P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 691.

<sup>4</sup> F. Ungváry and L. Markó, *Chem. Ber.*, 1972, **105**, 2457.

were measured by following the release of carbon monoxide during the reaction. Ellgen's data provided good evidence for the mechanism shown in equations (1)–(3). At high concentrations of complex, kinetic



evidence for formation of appreciable amounts of  $[\text{Co}_2(\text{CO})_7(\text{Ph}_2\text{C}_2)]$  was obtained. Ungváry and Markó's data for the reaction with hept-1-yne in toluene or n-heptane were also obtained at higher concentrations of complex and were consistent with rapid reversible formation of  $[\text{Co}_2(\text{CO})_7(\text{hept-1-yne})]$  followed by a slow irreversible step analogous to reaction (3).

Since these reactions are of interest in view of the importance of cobalt carbonyls as catalysts, and are related to our general interest in metal-metal bonded carbonyls, we have studied the corresponding reaction of hexacarbonylbis(tri-n-butylphosphine)dicobalt with diphenylacetylene. This is a much slower reaction than that of the octacarbonyl and this allows it to be followed by i.r. spectrophotometry with a consequently greater ease of detection of possible intermediates or side reactions. The substituted carbonyl is known to exist in solution<sup>5,6</sup> and in the solid state<sup>7,8</sup> in the purely Co-Co bonded form, *i.e.* without any bridging carbonyl groups.<sup>5</sup>

#### EXPERIMENTAL AND RESULTS

The complex  $[\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2]$  was prepared by the published method<sup>9</sup> and showed i.r. bands at 1 964w, 1 951vs, and 1 920w  $\text{cm}^{-1}$  in good agreement with published results.<sup>6</sup> Diphenylacetylene (Baker Chemicals) was used as received. Tri-n-butylphosphine (Baker Chemicals) was distilled under reduced pressure (16 cmHg) and stored under an atmosphere of nitrogen. Analysed mixtures of carbon monoxide and nitrogen were obtained from Matheson of Canada.

Manipulations involved in preparing solutions and in carrying out kinetic runs were exactly the same as those described previously<sup>1</sup> for a related study. The reaction was followed by monitoring the decreasing intensity of the band due to the complex at 1 951  $\text{cm}^{-1}$ . Reference cells were used that contained solutions of diphenylacetylene of the same concentration as those in the sample cells. Concentrations were corrected for expansion of decalin.

The reaction proceeded in two stages, the product of the first showing three bands of medium intensity (relative to the strong band of the original complex) at 2 059, 2 009, and 2 000  $\text{cm}^{-1}$ . These are in close agreement with the spectrum of the complex  $[(\text{OC})_3\text{Co}(\mu\text{-Ph}_2\text{C}_2)\text{Co}(\text{CO})_2(\text{PBU}_3)]$ , the first product of the reaction of tri-n-butylphosphine with  $(\mu\text{-C}_2\text{Ph}_2)\{\text{Co}(\text{CO})_3\}_2$ .<sup>1,10</sup> The second stage was accompanied by replacement of the above bands by three others of similar intensities at 2 013, 1 965, and 1 960  $\text{cm}^{-1}$ . This is consistent with formation of the complex  $(\mu\text{-Ph}_2\text{C}_2)\text{-}$

$\{\text{Co}(\text{CO})_2\text{PBU}_3\}_2$  through simple replacement of a carbon monoxide ligand by tributylphosphine released in the first stage. In spite of the very small concentration of the free phosphine, this reaction went to completion in the absence of added carbon monoxide. Under 1 atm carbon monoxide and *ca.*  $5 \times 10^{-4}\text{M}$ -complex an equilibrium mixture was obtained that contained *ca.* 60% of the bis(phosphine) acetylene complex, 40% of the phosphine acetylene complex, and no detectable unreacted  $[\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2]$ . (This corresponds to an equilibrium constant of *ca.* 40 for the interchange.) Only kinetic data for the first stage of the reaction will be reported here, those for the second stage having been described elsewhere.<sup>1</sup>

The reaction is retarded by carbon monoxide and all results reported here were obtained for reactions under a known pressure of carbon monoxide. In the absence of added tributylphosphine, pseudo-first-order rate constants increased with  $[\text{C}_2\text{Ph}_2]$  and became first order in  $[\text{C}_2\text{Ph}_2]$  above 0.1–0.2M. At lower concentrations pseudo-first-order rate plots were curved, the reaction slowing down appreciably as it proceeded. This effect was particularly marked for reactions under 1 atm carbon monoxide. Above  $[\text{C}_2\text{Ph}_2]$  *ca.* 0.1M rate plots were linear for *ca.* three half-lives. Average gradients over the first half-life were used to obtain rate constants from the curved rate plots. All rate constants are collected in Table 1.

TABLE 1

Pseudo-first-order rate constants for the reaction  $[\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2] + \text{C}_2\text{Ph}_2 \longrightarrow [\text{Co}_2(\text{CO})_5(\text{PBU}_3)(\text{C}_2\text{Ph}_2)] + \text{CO} + \text{PBU}_3$  in decalin at 100.0 °C.  $[\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2]$  *ca.*  $5 \times 10^{-4}\text{M}$

$p_{\text{CO}}/\text{atm}$	1.0	0.27	0.051	1.0
$10^3[\text{C}_2\text{Ph}_2]/\text{M}$	$10^4 k_{\text{obs}}^a / \text{s}^{-1}$			$10^4 k_{\text{obs}}^b / \text{s}^{-1}$
4.99			13.7	
9.31	1.40	6.35	21.0	
9.31	1.40	6.26		
11.5		7.22		
18.6	2.51			1.2
27.9	3.30	12.1		
46.6				2.94
70.4				3.02
93.1	8.05	21.5	53.7	
134				6.30
186	14.0	31.5	61.3	7.30
186			62.5	
279	15.1	36.3	75.4	8.80
466	24.5	50.2	110	13.4
610	25.4			
665		71.5		
705				17.4
839				18.2
858	34.0	79.7	157	

<sup>a</sup> No added  $\text{PBU}_3$ . <sup>b</sup>  $[\text{PBU}_3] = 2.27 \times 10^{-3}\text{M}$ .

The curvature of some of the rate plots suggests that the rate of reaction is reduced by the small amounts of phosphine released during the reaction and the effect of added phosphine is shown in Figure 1. Rate constants at the lowest value of  $[\text{PBU}_3]$  are those obtained in the absence of added phosphine, the concentration being estimated to be *ca.*  $1 \times 10^{-4}\text{M}$  from the extent of reaction corresponding to

<sup>5</sup> O. Vöhler, *Chem. Ber.*, 1958, **91**, 1235.

<sup>6</sup> A. R. Manning and J. R. Miller, *J. Chem. Soc. (A)*, 1970, 3352.

<sup>7</sup> J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423.

<sup>8</sup> R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

<sup>9</sup> F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc. (A)*, 1966, 1052.

<sup>10</sup> G. Cetini, O. Gambino, P. L. Stanghellini, and R. Rossetti, *Rend. Accad. Naz. XL*, 1968 [4], **18**, 45 (*Chem. Abs.*, 1970, **72**, 71104j).

where gradients of curved rate plots were measured. Although the effect even of very small amounts of phosphine was quite marked, rates of reaction did not decrease to zero at larger concentrations as might have been expected

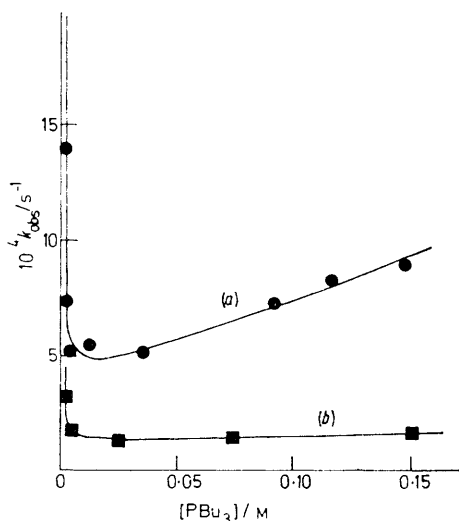


FIGURE 1 Variation of  $k_{\text{obs}}$  with  $[\text{PBu}_3]$  at  $p_{\text{CO}} = 1$  atm.  $[\text{C}_2\text{Ph}_2] = 0.186$  (●),  $0.028\text{M}$  (■)

but went to or through a minimum, the value and extent of which depended on the value of  $[\text{C}_2\text{Ph}_2]$  (Figure 1). The

TABLE 2

I.r. spectra ( $\text{cm}^{-1}$ ) of the complexes (a) $[\text{Co}_2(\text{CO})_5\text{L}_3]$ and (b) $[\text{Co}_2(\text{CO})_4\text{L}_4]$			
(a)	L = $\text{PMe}_3^a$	2 000m	1 947s(br)
	L = $\text{PET}_3^a$	1 992m	1 942s(br)
	L = $\text{PBu}_3^b$	1 997m	1 930s
(b)	L = $\text{PMe}_3^a$	1 939m	1 919vs
	L = $\text{PBu}_3^b$		1 910vs

<sup>a</sup> C. Pegot, M. Poilblanc, and F. Gallais, *Compt. rend.*, Ser. C, 1969, 268, 955. <sup>b</sup> Tentative assignment. The intensity of the band at  $1\,997\text{ cm}^{-1}$  changes with time in the same way as that of the band at  $1\,930\text{ cm}^{-1}$  but differently from that of the band at  $1\,910\text{ cm}^{-1}$ .

beginning of the minimum was found to coincide with the appearance of new bands in the i.r. spectra. These appear to be due to formation of the more highly substituted complexes  $[\text{Co}_2(\text{CO})_5(\text{PBu}_3)_3]$  and  $[\text{Co}_2(\text{CO})_4(\text{PBu}_3)_4]$  by direct attack on the bis(phosphine) complex. This would increase the rate of loss of complex over what would occur simply due to reaction with the acetylene. Thus, the new bands are closely related to those for the known complexes  $[\text{Co}_2(\text{CO})_5\text{L}_3]$  and  $[\text{Co}_2(\text{CO})_4\text{L}_4]$  (L =  $\text{PMe}_3$  and  $\text{PET}_3$ ), as

shown in Table 2. The occurrence of this side reaction makes very difficult a quantitative study of the inhibition by phosphine of the reaction with the acetylene. However, a series of runs under 1 atm carbon monoxide with  $[\text{PBu}_3] = 2.27 \times 10^{-3}\text{M}$  and variable  $[\text{C}_2\text{Ph}_2]$  showed similar behaviour to corresponding runs in the absence of added phosphine. The effect of the side reaction should be small at this low concentration of phosphine. Rate plots at low  $[\text{C}_2\text{Ph}_2]$  were no longer curved, in agreement with the conclusion that it was the phosphine released during the reactions in the absence of added phosphine that caused the curvature in these plots. These rate constants are also reported in Table 1.

## DISCUSSION

The rate data are consistent with there being two reaction paths, (A) and (B), the latter involving a first-order dependence on  $[\text{Ph}_2\text{C}_2]$  and the former a rise to a limiting rate  $k_a(\text{lim})$  with increasing  $[\text{Ph}_2\text{C}_2]$ . Thus the rate constants that showed a first-order dependence on  $[\text{C}_2\text{Ph}_2]$  were fitted to the rate equation  $k_{\text{obs}} = k_a(\text{lim}) + k_b[\text{C}_2\text{Ph}_2]$  by a least-squares program, in which the rate constants in a group of runs under the same pressure of carbon monoxide were assumed to have the same percentage uncertainty. Values of  $k_a(\text{lim})$  and  $k_b$  are given in Table 3. Standard deviations in  $k_a(\text{lim})$  and  $k_b$ , and in the individual values of the rate constants, have been corrected according to the numbers of degrees of freedom involved so that 95% confidence limits can be estimated by doubling the standard deviations. The numbers of degrees of freedom are small when the groups of rate constants are considered separately and so the uncertainties are rather large. However, standard deviations in  $k_{\text{obs}}$  do not appear to vary systematically from group to group and the assumption that the same value of  $\sigma(k_{\text{obs}})$  is common to all the rate constants results in a considerable increase in the number of degrees of freedom and a corresponding reduction in the uncertainties. These are the values shown in parentheses in Table 3.

Rate constants at lower values of  $[\text{C}_2\text{Ph}_2]$  were fitted to the rate equation  $k_{\text{obs}} - k_b[\text{C}_2\text{Ph}_2] = k_a = k_a(\text{lim}) - [\text{C}_2\text{Ph}_2]/(x + [\text{Ph}_2\text{C}_2])$ , characteristic of a reaction path in which the observed rate constant rises to a limiting rate at high values of  $[\text{C}_2\text{Ph}_2]$ . Plots of  $1/(k_{\text{obs}} - k_b[\text{C}_2\text{Ph}_2])$  against  $1/[\text{C}_2\text{Ph}_2]$  should be linear, the inverse of the intercept being  $k_a(\text{lim})$ . Such plots are shown in Figure 2 together with the intercept expected if the limiting value of the rate constant does equal the

TABLE 3

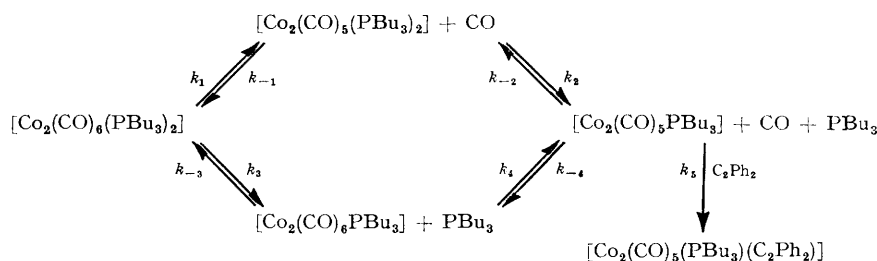
Rate parameters <sup>a</sup> obtained by least-squares analysis according to the rate equation  $k_{\text{obs}} = k_a(\text{lim}) + k_b[\text{C}_2\text{Ph}_2]$  from data for  $[\text{C}_2\text{Ph}_2] \geq 1.86 \times 10^{-2}\text{M}$

$10^3[\text{PBu}_3]_{\text{added}}$ M	$p_{\text{CO}}$ atm	$10^4[\text{CO}]^b$ M	$10^4 k_a(\text{lim})$ $\text{s}^{-1}$	$10^3 k_b$ $1\text{ mol}^{-1}\text{ s}^{-1}$	$\sigma(k_{\text{obs}})$ %
0	1.00	51.1	$7.78 \pm 2.20$ (1.14)	$3.05 \pm 0.58$ (0.29)	13.1 (6.6)
0	0.27	14.8	$16.5 \pm 3.2$ (2.6)	$7.56 \pm 0.84$ (0.67)	8.3 (6.6)
0	0.051	2.8	$34.7 \pm 4.2$ (4.4)	$14.8 \pm 1.3$ (1.4)	6.3 (6.6)
2.27	1.00	51.1	$3.93 \pm 0.88$ (0.60)	$1.82 \pm 0.23$ (0.16)	9.6 (6.6)

<sup>a</sup> Uncertainties are standard deviations. For details see text. <sup>b</sup> M. Basato and J. P. Fawcett, unpublished work; obtained by the method of T. J. Morrison and F. Billett, *J. Chem. Soc.*, 1948, 2033.

corresponding value of  $k_a(\text{lim})$  given in Table 3. The error bars correspond to the standard deviation calculated by assuming  $\sigma(k_{\text{obs}})$  to be 6.6% and using the appropriate standard deviation for  $k_b$  (Table 3). The data are, therefore, quite consistent with there being two paths as described.

**Mechanisms.**—*Path (A).* The difference between  $k_a(\text{lim})$  ( $p_{\text{CO}} = 1$  atm) at  $[\text{PBu}_3] = \text{ca. } 1 \times 10^{-4}$  and  $2.27 \times 10^{-3}\text{M}$  is  $(3.85 \pm 1.29) \times 10^{-4} \text{ s}^{-1}$ . This difference is almost certainly significant, being three standard deviations greater than zero. Allowance for any systematic error in the value at  $[\text{PBu}_3] = 2.27 \times 10^{-3}\text{M}$  would lead to an increase in this difference since the observed rates of loss of complex in the presence of phosphine are, if anything, enhanced by the occurrence of the side reaction leading to more highly substituted cobalt carbonyl. In addition to being decreased by added phosphine, the value of  $k_a(\text{lim})$  decreases substantially with increasing  $p_{\text{CO}}$ . It therefore appears probable that path (A) involves successive dissociation of both tributylphosphine and carbon monoxide before attack by the acetylene can occur. There is no *a priori* reason why dissociation first of phosphine and then of carbon monoxide should be more or less probable than the reverse order and the general mechanism shown in the Scheme below can be postulated.



SCHEME

A steady-state treatment in which  $[\text{Co}_2(\text{CO})_6\text{PBu}_3]$ ,  $[\text{Co}_2(\text{CO})_5(\text{PBu}_3)_2]$ , and  $[\text{Co}_2(\text{CO})_5\text{PBu}_3]$  are assumed to be reactive intermediates with a constant and small concentration leads to the rate equation (4) where  $\alpha = \{1 + (k_{-1}[\text{CO}]/k_2)\}/k_1$  and  $\beta = \{1 + (k_{-3}[\text{PBu}_3]/k_4)\}/k_3$ .

$$k_a = \frac{k_1 k_2 k_3 k_4 k_5 (\alpha + \beta) [\text{C}_2\text{Ph}_2]}{(k_1 k_2 k_3 k_4 \alpha + k_{-1} k_{-2} k_3 k_4 \beta) [\text{CO}] [\text{PBu}_3] + k_1 k_2 k_3 k_4 k_5 \alpha \beta [\text{C}_2\text{Ph}_2]} \quad (4)$$

At high values of  $[\text{C}_2\text{Ph}_2]$  this leads to a value of  $k_a(\text{lim})$  equal to  $(1/\alpha) + (1/\beta)$  so that  $k_a(\text{lim})$  should decrease with increasing  $[\text{CO}]$  and  $[\text{PBu}_3]$ . If the only dissociative sequence occurring in path (A) involves loss of carbon monoxide first followed by loss of phosphine then the rate equation is (5) and  $k_a(\text{lim})$  becomes equal

$$k_a = \frac{k_1 k_2 k_5 [\text{C}_2\text{Ph}_2]}{k_{-1} k_{-2} [\text{CO}] [\text{PBu}_3] + k_1 k_2 k_5 \alpha [\text{C}_2\text{Ph}_2]} \quad (5)$$

to  $1/\alpha$ , *i.e.* it should decrease with increasing  $[\text{CO}]$ , but not with increasing  $[\text{PBu}_3]$ , and a plot of  $1/k_a(\text{lim})$  against  $[\text{CO}]$  should be linear. If both dissociative

sequences occur then  $1/[k_a(\text{lim}) - 1/\beta]$  should be linearly dependent on  $[\text{CO}]$ . The fact that  $k_a(\text{lim})$  is decreased slightly as  $[\text{PBu}_3]$  is increased does suggest that initial dissociation of tributylphosphine occurs to some extent, although a reasonably good linear plot of  $1/k_a(\text{lim})$  against  $[\text{CO}]$  is obtained. A detailed quantitative analysis of the data shows that dissociation of phosphine from the complex  $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$  is at least ten times less probable than dissociation of carbon monoxide.

According to equation (5) the gradients of plots of  $1/k_a$  against  $1/[\text{C}_2\text{Ph}_2]$  should be proportional to  $[\text{CO}]$  and  $[\text{PBu}_3]$ . At  $[\text{PBu}_3] \text{ ca. } 1 \times 10^{-4}\text{M}$  the ratio of the gradients to the pressure of carbon monoxide is 49, 41, and 73  $\text{s mol}^{-1} \text{ atm}^{-1}$  for  $p_{\text{CO}} = 0.051, 0.27,$  and  $1.0$  atm, respectively, which is in satisfactory agreement with what is thought to be only an approximate rate equation if some initial phosphine dissociation does occur. On the other hand, the gradient is not nearly as sensitive to  $[\text{PBu}_3]$  as would be expected, increasing by a factor of only two for a 20-fold increase in  $[\text{PBu}_3]$ . It is not clear whether this is due to the approximate nature of the rate equation or to special difficulties associated with the side reaction of the complex with  $\text{PBu}_3$ , but the former is more probable since the side reaction is not likely to interfere significantly at the low values of  $[\text{PBu}_3]$ .

involved. It appears, therefore, that the dissociative path (A) proceeds mainly by loss of carbon monoxide followed by loss of  $\text{PBu}_3$ , but that the reverse order of ligand dissociation does contribute significantly, albeit to a much lesser extent.

This mechanism contrasts with that operating for the reaction of  $[\text{Co}_2(\text{CO})_8]$  with acetylenes in that two ligands have to dissociate from the complex, rather than only one, before attack by the acetylene can occur.\* The presence of the phosphine substituents could impose steric restraints on attack by the acetylene on the complexes  $[\text{Co}_2(\text{CO})_5(\text{PBu}_3)_2]$  or  $[\text{Co}_2(\text{CO})_6\text{PBu}_3]$  and the more basic nature of the phosphines could also reduce the electrophilic character of the four-co-ordinate cobalt

\* If only one ligand had to dissociate from the complex  $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$  before attack by acetylene could occur then  $k_a(\text{lim})$  would not be decreased at all by either added phosphine or carbon monoxide.

atom. On the other hand, when two ligands have dissociated, each cobalt atom is presumably in a planar, four-co-ordinate  $d^8$  configuration. Back-bonding through  $d_{xz}p_z$  hybrids to carbonyl or phosphine ligands lying along the  $x$  (Co-Co bond) axis would leave an empty  $d_{xz}p_x$  hybrid on each metal, directed in such a way as to be able to overlap well with the two orthogonal pairs of  $\pi$ -electrons on the acetylene if it approached the

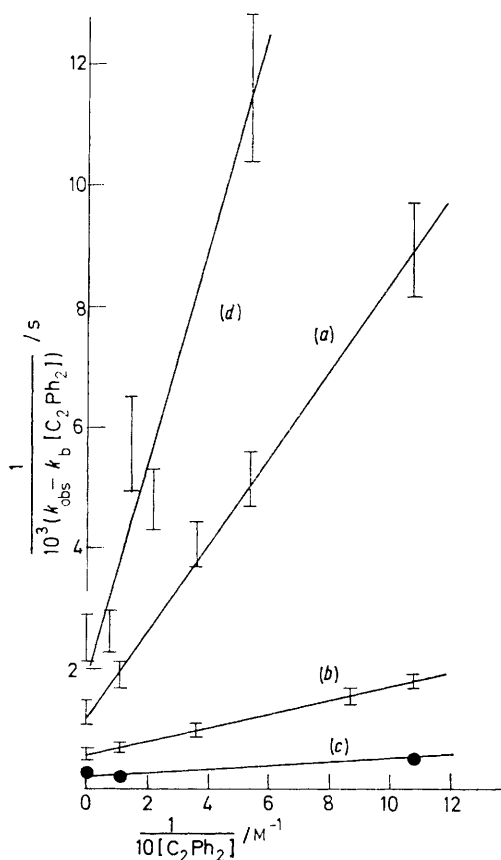


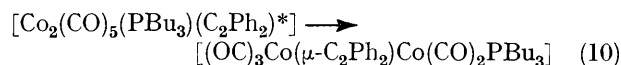
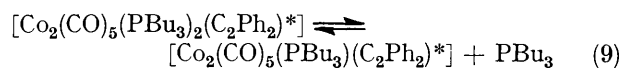
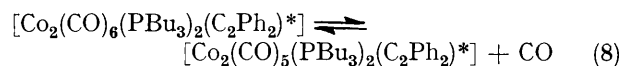
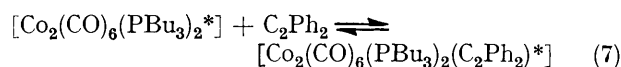
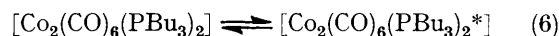
FIGURE 2 Variation of  $1/(k_{\text{obs}} - k_b[\text{C}_2\text{Ph}_2])$  with  $1/[\text{C}_2\text{Ph}_2]$ .  $p_{\text{CO}} = 1.0$  (a), 0.27 (b), 0.051 (c).  $([\text{PBu}_3] = \text{ca. } 1 \times 10^{-4}\text{M})$ , 1.0 atm. (d)  $([\text{PBu}_3] = 2.27 \times 10^{-3}\text{M})$ . Intercepts at  $1/[\text{C}_2\text{Ph}_2] = 0$  are values of  $1/k_a(\text{lim})$  taken from Table 3

reactive intermediate from above and with the  $\text{C}\equiv\text{C}$  axis perpendicular to the Co-Co axis.

*Path (B).* Path (B) is governed by an observed rate constant that is first order in  $[\text{C}_2\text{Ph}_2]$  but that also decreases with increasing  $[\text{CO}]$  and  $[\text{PBu}_3]$ . A plot of  $1/k_b$  against  $[\text{CO}]$  at constant  $[\text{PBu}_3]$  is linear with a finite intercept. Since there are only two different values of  $[\text{PBu}_3]$  it is not possible to say whether a plot of  $1/k_b$  against  $[\text{PBu}_3]$  is linear or not but it seems improbable that a power greater than unity in  $[\text{PBu}_3]$  is involved. The reaction must therefore proceed *via* reversible formation of several reactive intermediates. Since the rate of reaction is first order in  $[\text{C}_2\text{Ph}_2]$  over the whole range studied, the intermediate that is attacked by the acetylene must revert to its precursor much more readily than it is attacked by the acetylene.

The retardation in the rate of reaction by both carbon monoxide and phosphine suggests that reversible dissociation of these ligands also occurs. The values obtained above for the limiting rates of dissociation of either carbon monoxide or phosphine from the complex  $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$  are too small for these to account for the initial processes in path (B) and in any case these dissociative processes have already been assigned to path (A). It seems, therefore, that it is the complex  $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2]$  itself that reversibly forms the reactive intermediate attacked by the acetylene, and that reversible dissociation of carbon monoxide and phosphine occur subsequently.

It can be shown that the reaction sequence shown in equations (6)–(10) leads to the rate equation  $k_{\text{obs}} = p[\text{C}_2\text{Ph}_2]/(1 + q[\text{CO}] + r[\text{CO}][\text{PBu}_3] + w[\text{C}_2\text{Ph}_2])$ ,



where  $p$ ,  $q$ , and  $r$  are complicated combinations of rate constants for the individual steps and  $w$  is, in addition, a function of  $[\text{CO}]$  and  $[\text{PBu}_3]$ . Provided that  $w[\text{C}_2\text{Ph}_2]$  is always negligible compared with the rest of the denominator, our data for path (B) are quite consistent with this rate equation. A simple analysis of the data leads to the values  $p = 2.0 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $q = 1.0 \times 10^{-3} \text{ l mol}^{-1}$ , and  $r = 3.9 \times 10^5 \text{ l}^2 \text{ mol}^{-2}$ , from which set the calculated values  $10^3 k_b = 3.2, 8.1, 15.7$ , and  $1.9 \text{ l mol}^{-1} \text{ s}^{-1}$  are obtained, in excellent agreement with the appropriate experimental values listed in Table 3.

If the phosphine ligand dissociates from the reactive intermediate before carbon monoxide then  $q[\text{CO}]$  must be replaced by  $q[\text{PBu}_3]$  in the above rate equation. However, this sequence cannot in fact operate alone since an analysis of the data then leads to negative values of  $q$ . A small contribution of this sequence, as in path (A), could be occurring as might other modifications of the relatively simple mechanism shown in equations (6)–(10). Much more extensive data would be necessary to elucidate details of any more complex mechanism and these would be difficult to obtain for reasons already discussed.

The reactive species  $[\text{Co}_2(\text{CO})_6(\text{PBu}_3)_2^*]$  must have a site at which the acetylene can attack and it can conveniently be formulated as  $[\text{PBu}_3(\text{OC})_3\text{Co-CO-Co}(\text{CO})_2\text{-PBu}_3]$  formed by metal migration<sup>11</sup> of one cobalt atom

<sup>11</sup> L. I. B. Haines, D. Hopgood, and A. J. Poë, *J. Chem. Soc. (A)*, 1968, 421; D. DeWit, J. P. Fawcett, A. J. Poë, and M. V. Twigg, *Co-ordination Chem. Rev.*, 1972, 8, 81.

on to the carbon atom of a carbon monoxide ligand attached to the other. This is the same intermediate as was proposed for thermal insertion, in tetrahydrofuran, of tin(II) chloride into the Co-Co bond of this complex.<sup>12</sup> The fact that tin(II) chloride competes much more successfully than the acetylene for this intermediate can be ascribed to the much higher nucleophilic character expected for tin(II) chloride, although

the different solvents used for the two studies may also be important.

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<sup>12</sup> P. F. Barrett and A. J. Poë, *J. Chem. Soc. (A)*, 1968, 429.

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