Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part IV.[1] The Substitution Reaction of μ-Diphenylacetylene-bis(tetracarbonylcobalt) with Tri-n-butylphosphine

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μ-Diphenylacetylene-bis(tetracarbonylcobalt) undergoes two successive substitution reactions with tri-n-butylphosphine in decalin and the kinetics of these reactions have been studied. Each step shows pseudo-first-order behaviour with $k_{\mathrm{obs}} = k_1 + k_2[\mathrm{PBu_3}]$ under an atmosphere of argon. Activation parameters have been obtained for each path in each step and the effect of carbon monoxide on the paths governed by k_1 is consistent with a CO-dissociative mechanism. Relative rate constants for bimolecular attack on the co-ordinatively unsaturated intermediates by carbon monoxide and tributylphosphine have been obtained. The rate parameters for the two dissociative paths are quite similar but the second bimolecular path is governed by a much higher value of $\Delta H^‡$, and a much less negative value of $\Delta S^‡$, than the first.

μ-DIPHENYLACETYLENE-BIS(TETRACARBONYLCOBALT) is a metal–metal bonded carbonyl similar in structure to the bridged form of cobalt octacarbonyl but with the two bridging carbonyl groups replaced by the diphenylacetylene molecule.[2] This complex undergoes CO-exchange[3] reactions much more slowly than cobalt carbonyls that contain one or more bridging carbonyl groups[4] and a study of the kinetics of its substitution reactions seemed likely to be of interest as part of a general study of reaction mechanisms of metal–metal bonded carbonyls[1] and as a further example of reactions of metal carbonyls containing an unsaturated hydrocarbon. We report here a complete study of its reaction in decalin with tri-n-butylphosphine. An earlier, partial study has been reported[5] of the first stage of the reaction in n-heptane as followed by measurement of the rate of release of ^{14}CO from the complex. The conclusions reached differ substantially from ours.

EXPERIMENTAL

$[\mathrm{Co_2(CO)_6(C_2Ph_2)}]$ was prepared from cobalt octacarbonyl (Strem Chemicals) by the published method.[6] I.r. spectrum in decalin: 2 092m, 2 059s, 2 030s, 2 027s, and 2 010m cm^{-1} (*cf.* spectrum in n-hexane: 2 091m, 2 056s, 2 030s, 2 027s, and 2 013w cm^{-1}).[7] Tri-n-butylphosphine (Baker Chemicals) was distilled under reduced pressure (16 cmHg) and stored under an atmosphere of nitrogen before use. Decalin (Baker Analysed Reagent) was stored over molecular sieves.

Experimental Procedures.—Solutions of the phosphine were prepared with care taken to avoid reaction with oxygen by continuously flushing the equipment used with nitrogen. The solutions were finally deoxygenated by freeze-pump-thaw cycles and transferred under an atmosphere of argon to the reaction vessel containing known amounts of solid complex. The vessels used were sealed with rubber septum caps and transfer through stainless-steel tubing, inserted through the caps, was effected by applying a suitable pressure of argon. The reaction vessels were wrapped in aluminium foil and immersed in an oil-bath thermostatted within ±0·1 °C. Aliquot portions were removed periodically, through stainless-steel tubing, by an applied pressure of argon, and rapidly cooled in ice, their i.r. spectra being measured when convenient with a Perkin-Elmer 257 spectrophotometer. The solubility of carbon monoxide in decalin was measured[8] by the method of Morrison and Billet.[9]

RESULTS

The reaction proceeds in two clearly separated stages, the first being characterised by the growth of i.r. bands at 2 059m, 2 009m, 2 001m, 1 990vw, and 1 960w cm^{-1}, and the second by decay of these bands and formation of others at 2 013m, 1 965m, and 1 960m cm^{-1}. (The intensities are indicated relative to the bands in the reactant complex.) Apart from the weak bands at 1 990 and 1 960 cm^{-1}, these spectra are in close agreement with those observed by Cetini *et al.*[5] for the isolated complexes $[\mathrm{(OC)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_2PBu_3}]$ and $(\mu\text{-}\mathrm{C_2Ph_2})[\mathrm{Co(CO)_2PBu_3}]_2$, respectively, and the reaction therefore consists of successive formation of these mono- and bis-substituted derivatives.

The rate of the first stage was measured by following the decreasing absorbance of the bands at 2 030 or 2 092 cm^{-1} due to the complex $(\mu\text{-}\mathrm{C_2Ph_2})[\mathrm{Co(CO)_3}]_2$, and that of the second by following the decreasing absorbance of the band at 2 059 cm^{-1} due to $[\mathrm{(OC)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_2PBu_3}]$. Good linear pseudo-first-order plots were generally obtained over 3—4 half-lives but, when $[\mathrm{PBu_3}]$ was greater than *ca.* 0·4M, an initial rapid reaction was observed for the first stage after which first-order rates became consistent with the pattern established at lower concentrations. This effect was most pronounced at 25 °C and was not observed at higher temperatures. It was also observed in reactions under an atmosphere of carbon monoxide at 40 °C.

Both stages of the reactions under an atmosphere of argon followed the rate equation $k_{\mathrm{obs}}(\mathrm{Ar}) = k_1 + k_2[\mathrm{PBu_3}]$, although values of $k_{\mathrm{rbs}}(\mathrm{Ar})$ for the second stage tended to be low at values of $[\mathrm{PBu_3}]$ below *ca.* 0·05M. This stage is particularly sensitive to the presence of carbon monoxide and these low values are consistent with retardation caused by carbon monoxide released during the substitution. When the reactions were followed under 1 atm carbon

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TABLE 1

Observed pseudo-first-order rate constants for the reactions $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3] + PBu_3 \longrightarrow [L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2PBu_3] + CO$ in decalin. $[\text{Complex}] = (5\text{—}15) \times 10^{-4}$M

L = CO

$10^2[PBu_3]$ / M	$10^5k_{obs}(Ar)$ / s^{-1}	$10^5k_{obs}(CO)$ [a] / s^{-1}
	t = 25 °C	
5·15	8·88	
14·8	28·2	
28·8	53·7	
49·1	87·7	
71·3	126	
71·4	134	
89·8	186	
	t = 40 °C	
1·05	7·33	5·71
4·91	27·4	26·0
14·8	79·2	79·7
30·1	170	
30·2		165
45·4	240	245
	t = 55 °C	
1·11	37·2	21·8
4·85	83·0	76·4
14·4	214	206
29·1	396	
49·7	690	
	t = 70 °C	
0·62	223	77·0
2·02	269	165
2·02	268	
4·91		280
8·28	481	433
14·3	700	660
21·4	930	845
29·4	1 170	1 120

L = PBu_3

$10^2[PBu_3]$ / M	$10^5k_{obs}(Ar)$ / s^{-1}	$10^5k_{obs}(CO)$ [a] / s^{-1}
	t = 55 °C	
1·11	8·9 [b]	1·91
4·85	10·3 [b]	5·25
14·4	11·9	8·75
29·1	13·4	
49·7	15·4	
62·7	17·0	16·8
	t = 70 °C	
0·62	83·0 [b]	10·9
2·02	80·0 [b]	29·6
4·79	79·0 [b]	46·2
8·28	93·0	66·6
14·3	94·4	83·5
21·4	101	92·4
29·4	106	97·5
44·1	112	107
59·0	125	
60·0		125
76·2	133	130
	t = 85 °C	
1·01	490 [b]	104
4·71	590 [b]	324
14·0	670	
14·1	638	495
27·2	700	
46·4	775	
67·3	790	
84·6	890	
87·7		845

Reactions under 1 atm carbon monoxide. [b] Low values, not used in computation of k_1 and k_2.

monoxide values of k_{obs} decreased essentially to zero at very low values of $[PBu_3]$ although even the slowest reactions followed went to completion. This effect was much more clearly shown by the second stage for which the second-order path governed by k_2 was relatively much less pronounced. Values of k_{obs} are collected in Table 1.

DISCUSSION

The kinetic data are consistent with both substitution reactions proceeding by concurrent dissociative and associative paths according to the reaction scheme shown below (L = CO for the first stage and PBu_3 for the second). The rate equation for this scheme is given by (1) which becomes $k_{obs} = k_1 + k_2[PBu_3]$ in

$$\begin{tikzcd}
{[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]} \arrow[rr, "k_2", "+PBu_3"'] \arrow[dr, shift left, "k_1"] & & {[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2PBu_3] + CO} \\
& {[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2] + CO} \arrow[ul, shift left, "k_{-1}"] \arrow[ur, "k_3", "+PBu_3"'] &
\end{tikzcd}$$

$$k_{obs} = \{(k_1k_3[PBu_3]/k_{-1}[CO])/(1 + k_3[PBu_3]/k_{-1}[CO])\} + k_2[PBu_3] \quad (1)$$

the absence of appreciable amounts of carbon monoxide. Equation (1) can be rearranged to give (2) so that linear

$$1/(k_{obs} - k_2[PBu_3]) = (1/k_1) + (k_{-1}[CO]/k_1k_3[PBu_3]) \quad (2)$$

plots of $1/(k_{obs} - k_2[PBu_3])$ against $1/[PBu_3]$ should be obtained, and values of k_1 and k_{-1}/k_3 be derivable therefrom. Good linear plots are indeed obtained from the data for the second stage but those for the first stage are satisfactory only for the reaction at 70 °C when the dissociative path becomes relatively more pronounced than at lower temperatures. A very approximate value of k_{-1}/k_3 can be obtained for the first stage at 55 °C, however, by using the value of k_1 obtained from the reactions under an atmosphere of argon. Values of k_1, k_2, and k_{-1}/k_3 are given in Tables 2 and 3 together with the corresponding activation parameters. Values of k_1 and k_2 in Table 2 were obtained by linear weighted least-squares analysis of the dependence of $k_{obs}(Ar)$ on $[PBu_3]$, each value of $k_{obs}(Ar)$ being assumed to have the same percentage standard deviation at a given temperature. Where possible, values of k_1 and k_{-1}/k_3 were also obtained by weighted least-squares analysis of the values of $k_{obs}(CO)$ by making use of equation (2) and the appropriate values of k_2 found from the reactions under an atmosphere of argon. In all cases values of $1/\{k_{\mathrm{obs}}(\mathrm{CO}) - k_2[\mathrm{PBu_3}]\}$ were weighted in accordance with standard deviations calculated from those already found for $k_{\mathrm{obs}}(\mathrm{Ar})$ and k_2 (Table 2). All the uncertainties listed are standard deviations that have been corrected for the number of degrees of freedom, so that estimates of the 95% confidence limits can be obtained by doubling the uncertainties. The standard deviations of $k_{\mathrm{obs}}(\mathrm{Ar})$ seem to show trends with varying temperature but the significance of these trends is not obvious. The agreement between the two sets of values for k_1 is good, the differences being statistically insignificant in two cases and probably ascribable to relatively small systematic errors in the other two. The two sets of values of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ for L = $\mathrm{PBu_3}$ are also in excellent agreement.

TABLE 2

Kinetic parameters[a] obtained from the rate equation $k_{\mathrm{obs}}(\mathrm{Ar}) = k_1 + k_2[\mathrm{PBu_3}]$ for the reactions $[\mathrm{L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3}] + \mathrm{PBu_3} \longrightarrow [\mathrm{L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2PBu_3}] + \mathrm{CO}$

t/°C	$10^5\,k_1$/s^{-1}	$10^4\,k_2$/l mol^{-1} s^{-1}	$\sigma(k_{\mathrm{obs}})$/%
	L = CO		
25·0		18·9 ± 0·7	7·5
40·0	1·70 ± 0·43	53·3 ± 1·6	5·2
55·0	22·2 ± 1·8	131 ± 4	4·5
70·0	201 ± 3	338 ± 5	1·8

$\Delta H_1^{\ddagger}$ = 136·3 ± 4·2 kJ mol^{-1} (32·6 ± 1·0 kcal mol^{-1})
$\Delta S_1^{\ddagger}$ = 100 ± 13 J K^{-1} mol^{-1} (24·0 ± 3·0 cal K^{-1} mol^{-1})
$\Delta H_2^{\ddagger}$ = 52·0 ± 0·6 kJ mol^{-1} (12·45 ± 0·15 kcal mol^{-1})
$\Delta S_2^{\ddagger}$ = −122 ± 2 J K^{-1} mol^{-1} (−29·3 ± 0·5 cal K^{-1} mol^{-1})

t/°C	$10^5\,k_1$/s^{-1}	$10^4\,k_2$/l mol^{-1} s^{-1}	$\sigma(k_{\mathrm{obs}})$/%
	L = $\mathrm{PBu_3}$		
55·0	10·4 ± 0·3	1·04 ± 0·07	1·8
70·0	87·2 ± 1·3	6·08 ± 0·36	1·8
85·0	612 ± 23	30·8 ± 5·1	4·2

$\Delta H_1^{\ddagger}$ = 130·0 ± 1·7 kJ mol^{-1} (31·1 ± 0·4 kcal mol^{-1})
$\Delta S_1^{\ddagger}$ = 75 ± 4 J K^{-1} mol^{-1} (18·0 ± 1·2 cal K^{-1} mol^{-1})
$\Delta H_2^{\ddagger}$ = 107·4 ± 4·2 kJ mol^{-1} (25·7 ± 1·0 kcal mol^{-1})
$\Delta S_2^{\ddagger}$ = 6 ± 13 J K^{-1} mol^{-1} (1·5 ± 3·0 cal K^{-1} mol^{-1})

[a] Uncertainties are standard deviations (see text).

TABLE 3

Kinetic parameters[a] obtained from the rate equation $k_{\mathrm{obs}}(\mathrm{CO}) - k_2[\mathrm{PBu_3}] = (k_1k_3[\mathrm{PBu_3}]/k_{-1}[\mathrm{CO}])/(1 + k_3[\mathrm{PBu_3}]/k_{-1}[\mathrm{CO}])$[b]

t/°C	$10^4\,k_1$/s^{-1}	k_{-1}/k_3
	L = CO	
40·0		
55·0		*ca.* 4
70·0	(16·0 ± 0·6)	2·13 ± 0·16
	L = $\mathrm{PBu_3}$	
55·0	1·01 ± 0·03	9·15 ± 0·44
70·0	9·55 ± 0·13	8·95 ± 0·24
85·0	62·6 ± 3·7	9·58 ± 0·97

$\Delta H_1^{\ddagger}$ = 134·7 ± 1·7 kJ mol^{-1} (32·2 ± 0·4 kcal mol^{-1})
$\Delta S_1^{\ddagger}$ = 88·8 ± 5·0 J K^{-1} mol^{-1} (21·2 ± 1·2 cal K^{-1} mol^{-1})
$\Delta H_{-1}^{\ddagger} - \Delta H_3$ = 0·015 ± 2·9 kJ mol^{-1} (0·004 ± 0·686 kcal mol^{-1})
$\Delta S_{-1}^{\ddagger} - \Delta S_3^{\ddagger}$ = 18·5 ± 8·4 J K^{-1} mol^{-1} (4·4 ± 2·0 cal K^{-1} mol^{-1})

[a] Uncertainties are standard deviations (see text); the standard deviations take into account the covariance of the parameters $1/k_1$ and k_{-1}/k_1k_3 obtained from least-squares analysis according to equation (2). [b] Values of k_2 from Table 2.

Our interpretation of the results differs substantially from that proposed by Cetini *et al.*[5] from a study of the first stage only. They concluded that their data showed k_{obs} to rise with $[\mathrm{PBu_3}]$ from zero to a limiting rate at high values of $[\mathrm{PBu_3}]$ rather than to increase linearly with $[\mathrm{PBu_3}]$ from a finite value at $[\mathrm{PBu_3}] = 0$. This was thought to suggest reversible formation of a reactive intermediate form of the complex, without loss of any ligands, the intermediate then undergoing irreversible reaction with $\mathrm{PBu_3}$ to form the product. In fact, their data can be analysed in terms of our rate law in which case we obtain $k_1 = (1\cdot7 \pm 0\cdot2) \times 10^{-5}$ s^{-1} and $k_2 = (2\cdot1 \pm 0\cdot3) \times 10^{-3}$ l mol^{-1} s^{-1} for the substitution reaction in n-heptane at 32 °C as compared with a value of $1\cdot6 \times 10^{-5}$ s^{-1} for the CO-exchange rate constant obtained under the same conditions in the earlier study by Cetini *et al.*[3] By extrapolation, our data lead to values of $k_1 = (0\cdot47 \pm 0\cdot07) \times 10^{-5}$ s^{-1} and $k_2 = 2\cdot9 \times 10^{-3}$ l mol^{-1} s^{-1} for substitution at 32 °C in decalin and this agreement can be considered to be quite good in view of the extrapolation involved, the different solvent used, and the different techniques employed.

Values of $\Delta S_1^{\ddagger}$, for the first and second stages, together with the nature of the retardation of the rate by carbon monoxide, are in good agreement with reversible, CO-dissociative mechanisms for the paths governed by k_1.[10] By contrast, rate parameters reported for the first-order reaction of triphenylphosphine with the complex $(\mu\text{-}\mathrm{C_2H_2})[\mathrm{Co(CO)_3}]_2$ in toluene[11] are not consistent with a simple dissociative path. The rates and activation enthalpies for dissociative substitution in the diphenylacetylene complex are very much less favourable than the parameters for substitution[11] or exchange[12] in cobalt carbonyl itself[11] or in the complex $[\mathrm{Co_2(CO)_7(C_7H_8O_2)}]$.[13] The latter contains one bridging carbonyl group and a bridging sp^3 hybridised carbon that forms part of a lactone ring.[14] The bridging acetylene clearly stabilises the molecule towards dissociative substitution. The absence of a bridging carbonyl group[4] cannot by itself explain this since the complex $(\mu\text{-}\mathrm{GePh_2})(\mu\text{-}\mathrm{CO})[\mathrm{Co(CO)_3}]_2$, in which a $\mathrm{GePh_2}$ bridge has replaced one of the bridging carbonyls in $\mathrm{Co_2(CO)_8}$,[15] is also relatively inert to dissociative substitution.[16]

The close similarity of the two values of $\Delta H_1^{\ddagger}$ shows that there is only a small effect transmitted by the phosphine introduced in the first stage on the dissociation of carbon monoxide from the other

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cobalt atom in the second stage. In contrast to this the effect of the introduction of the first phosphine on the rate parameters for bimolecular substitution is very pronounced. The values of $\Delta H_2^‡$ and $\Delta S_2^‡$ for the first stage are characteristic of an S_N2 mechanism in which attack on the metal occurs and for which the ratio of bond-making to bond-breaking is probably quite high.[17,18] The parameters are very similar to those for the bimolecular reaction of tributylphosphine with the complex $Ru_3(CO)_{12}$[18] and of triphenylphosphine with $[Co(CO)_3NO]$.[17] It is, of course, possible in principle that the second-order path involves formation of a reactive form of the complex $(\mu\text{-}C_2Ph_2)[Co(CO)_3]_2$ which reverts to the less-reactive form much more rapidly than it is attacked by tributylphosphine to form products. The transition states for both these mechanisms could involve a high degree of $Co\text{-}PBu_3$ bonding and the distinction be simply one of whether the complex rearranges itself into a form suited to bimolecular attack by phosphine *before* the attack occurs or *during* the process of attack. These two mechanisms can be distinguished only in those cases where reversion of the reactive intermediate to the more stable form occurs at a rate comparable to the rate of attack by the nucleophile to form the products. In this case k_{obs} will rise to a limiting value at high concentration of nucleophile. There is some evidence that this might occur in the reaction of triphenylphosphine with the complex $Co_2(CO)_8$.[11] It may be that the unusual behaviour at low temperature and high values of $[PBu_3]$ reported above is also associated with formation of some sort of reactive species, the nature of which is not clear.

Although a few cases of bimolecular S_N2 attack on the metal in binary carbonyl complexes are believed to exist,[18,19] most such reactions occur[17] with carbonyl complexes in which the metal has an ill defined oxidation state. Associated with this ambiguous oxidation state is a built-in flexibility in their electronic structure that enables them to respond readily to the approach of a nucleophile. The complex $(\mu\text{-}C_2Ph_2)[Co(CO)_3]_2$ fits into this category since the bonding of the acetylene to the two cobalt atoms is electronically not at all clearly defined[2] and the acetylene molecule can easily be envisaged as being able to accept more electrons from the cobalt atoms under stress of the approaching nucleophile.

The fact that the values of $\Delta H_2^‡$ and $\Delta S_2^‡$ for the second stage are, respectively, much higher and much less negative than those for the first suggests either that bond-making in the transition state of this stage is much less pronounced, or that the molecule has to ' loosen up ' much more in order for extensive bond-making to occur. This could be due to steric and/or electronic effects. The size of the phosphine ligand[20] already present in the complex might make approach of a second such ligand more difficult, and its greater basicity[17] (compared with carbon monoxide) could result in greater back-donation to the acetylene so that the latter's capacity to accept still more electron density as the second phosphine approaches is correspondingly reduced. The importance of steric effects in bimolecular substitutions of metal carbonyls is well established, for example, in the substitution of triphenylphosphine into the complexes $Ru_3(CO)_{12}$,[18] $Mo(CO)_6$ and $W(CO)_6$,[18,19] and of tricyclohexylphosphine into $[Co(CO)_3NO]$ and $[(\eta^5\text{-}C_5H_5)Rh(CO)_2]$.[17]

The ratios of the rate constants for bimolecular attack by carbon monoxide and tributylphosphine on the co-ordinatively unsaturated intermediates involved in the dissociative paths are not greatly different, both showing that carbon monoxide attacks the vacant site somewhat more readily than does the phosphine. This is the reverse of what is normally found for bimolecular attack at co-ordinatively saturated centres towards which carbon monoxide appears to be a weak nucleophile while tri-n-butylphosphine is one of the strongest.[17] Very few relative rate constants for attack at co-ordinatively unsaturated centres are available. Systematic studies of such relative rate parameters might well provide a way of assessing the nature of the co-ordinatively unsaturated intermediate.

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