Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part VI.[1] Reactions of μ-Carbonyl-μ-diphenylgermanediyl-bis(tricarbonylcobalt) with Carbon Monoxide, Triphenylphosphine, and Tri-n-butylphosphine

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The reversible ' ring-opening ' reaction of the complex $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$, (I), with carbon monoxide in decalin to form $(\mu\text{-}GePh_2)\{Co(CO)_4\}_2$, (II), proceeds by a path first order in [Complex] and [CO], and the reverse reaction is first order only in [Complex]. Activation and equilibrium parameters have been obtained. Reaction with triphenylphosphine forms the complex $(\mu\text{-}GePh_2)\{Co(CO)_3L\}_2$, (III; L = PPh_3), probably *via* $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$, produced in a rate-determining CO-dissociative process and subsequently attacked by a second phosphine molecule in a rapid ring-opening reaction. Bimolecular attack by triphenylphosphine also occurs and leads directly to the complex $(\mu\text{-}GePh_2)\{Co(CO)_3L\}\{Co(CO)_4\}$, (IV; L = PPh_3). Reaction of the latter with triphenylphosphine produces complex (III; L = PPh_3) by a process first order only in [Complex]. Reaction of complex (II) with triphenylphosphine proceeds *via* rate-determining formation of (I) which then reacts rapidly with the phosphine as described above. Tri-n-butylphosphine can attack the complexes (II) and (IV; L = PBu_3) by bimolecular processes. The mechanisms of these reactions are discussed in terms, especially, of relative rate constants for bimolecular attack by carbon monoxide and triphenylphosphine on the complexes or reactive intermediates involved.

μ-CARBONYL-μ-DIPHENYLGERMANEDIYL-BIS(TRICARBONYLCOBALT), (I), is an analogue of dicobalt octacarbonyl that appears to contain a bridging diphenylgermanediyl group in place of one of the bridging carbon monoxide ligands.[2] Since the diphenylgermanediyl group is not known to be able to bond only to one metal atom in a carbene-like way, the complex should exist only in the form in which the cobalt–cobalt bond is supported by two bridging groups. The complex undergoes reaction with carbon monoxide to form diphenylbis(tetracarbonylcobalt)germanium(IV), (II),[2,3] in what can be called a ring-opening process of a type

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[1] Part V, M. Basato and A. J. Poë, *J.C.S. Dalton*, 1974, 607.

[2] S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Comm.*, 1969, 1297.

[3] E. H. Brooks and W. A. G. Graham, Abs. Fourth Internat. Conf. Organometallic Chem., Bristol, 1969, A2; personal communication.

that is now quite well established.[3,4] Reaction with triphenylphosphine has also been shown to lead to ring opening with formation of diphenyl(tetracarbonylcobalt)(tricarbonyltriphenylphosphinecobalt)germanium(IV), (IV).[3] In view of the relative novelty of these complexes and their reactions, and of the scarcity of mechanistic studies on bridged metal–metal bonded carbonyls, we have studied the kinetics of reaction of complex (I) with carbon monoxide, triphenylphosphine, and tri-n-butylphosphine, and those of (II) and (IV; L = PPh_3 or PBu_3) with L.

EXPERIMENTAL AND RESULTS

Chemicals.—The complex μ-carbonyl-μ-diphenylgermanediyl-bis(tricarbonylcobalt), (I), was prepared from dicobalt octacarbonyl (Strem Chemicals) and diphenylgermane (K and K Laboratories, Inc.) according to the published method.[2,5] The product gave i.r. spectra (Table 1) and kinetic parameters identical to those from a fully characterised sample[5] kindly provided by Dr. S. A. Fieldhouse. The complex diphenylbis(tetracarbonylcobalt)germanium(IV), (II), was prepared *in situ* in decalin by treating solutions (*ca.* 10^{-3}M) of (I) with carbon monoxide (*ca.* 100 p.s.i.) at 80 °C for 5 h in a 100 cm³ Fischer–Porter glass pressure vessel. The higher the pressure and the lower the temperature the better the yield, *ca.* 90% conversion occurring under the above conditions. The mono- and bis-phosphine complexes $(\mu\text{-}GePh_2)\{Co(CO)_3L\}\{Co(CO)_4\}$ (IV) and $(\mu\text{-}GePh_2)\{Co(CO)_3L\}_2$ (III) (L = PPh_3 and PBu_3) were formed as products of the reaction of either complexes (I) or (II) with the appropriate phosphine. They were identified in solution by their i.r. spectra (Table 1), which were measured with a Perkin-Elmer 257 spectrophotometer in matched 0·1 mm path-length cells with sodium chloride windows.

TABLE 1

Carbonyl stretching frequencies (cm^{-1}) of some μ-diphenylgermanediyl derivatives of cobalt carbonyls in decalin (relative absorption coefficients in parentheses)

$[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$, (I)	2 092 (5·2)	2 052 (10)	2 032 (8·7)	2 014 (6·2)	1 834 (3·0)		
(I) [a]	2 089 (7·2)	2 064 (10)	2 033 (9·3)	2 016 (7·8)	1 839 (6·0)		
$[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_4]$, (II)	2 100 (2·2)	2 084 (9·1)	2 032 (7·2)	2 022 (10)	2 014 (8·8)	1 997 (6·2)	
(II) [a]	2 103 (4·4)	2 086 (9·4)	2 036 (8·9)	2 026 (10)	2 020 (9·6)	2 002 (7·6)	
$[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3L]$, (IV; L = PPh_3)	2 089 (6·9)	2 037 (2·4)	2 025 (4·2)	2 012 (10)	1 998 (8·6)	1 976 (5·5)	1 967 (7·6)
(IV; L = PPh_3) [b]	2 084s	2 031m	2 019m	2 003s	1 988s	1 963m	1 938w
(IV; L = PBu_3) [c]	2 084 (5·9)	2 027 (3·7)	2 018 (4·1)	2 007(10)	1 993 (9·0)	1 961 (6·9)	1 949 (9·3)
$[L(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_3L]$, (III; L = PPh_3) [d]	2 040 (0·2)	2 022 (1·1)	1 976 (10)	1 967 (7·0)	1 949 (5·0)		
(III; L = PBu_3)	2 022 (0·6)	2 002 (1·2)	1 961 (10)	1 951 (9·5)	1 894 (2·9)		

[a] In hexane, ref. 5. [b] In benzene; W. A. G. Graham and E. H. Brooks, personal communication. [c] Not isolated but characterised by comparison of its spectrum with that of complex (IV; L = PPh_3). [d] Not isolated but complex (III; L = PBu_3) has been isolated and characterized: A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Comm.*, 1971, 155; A. J. Cleland, Ph.D. Thesis, University of Toronto, 1972.

Triphenylphosphine (B.D.H.) was recrystallised from ethanol and dried under vacuum, and tri-n-butylphosphine (Baker Chemicals) was distilled under reduced pressure (16 cmHg) before use. Argon (99·998%) and carbon monoxide (C.P. grade, 99·5%) were obtained from Union Carbide of Canada Ltd. Cylinders of gas mixtures ($CO-N_2$) of known composition (±2%) were obtained from Matheson of Canada. Decalin (Baker Analysed Reagent) was stored over molecular sieves.

Kinetic Procedures.—Complex (I) was kept in the dark in a nitrogen-filled dry-box throughout. For kinetic runs small portions were transferred, in the dry-box, to foil-wrapped Schlenk tubes which were sealed with rubber septum caps. Solutions of the phosphines were deoxygenated in another similarly sealed Schlenk tube by two or three freeze-pump-thaw cycles and transferred to the reaction vessel through stainless-steel tubing by applying a positive pressure of the appropriate gas. The complex was quickly dissolved by shaking, the reaction vessel was transferred to an oil-bath (±0·1 °C), and aliquot portions were removed through stainless-steel tubes at appropriate times. For reactions below *ca.* 80 °C, aliquot portions were ejected directly into an i.r. cell and spectra scanned immediately in the C–O stretching region. For reactions at higher temperatures aliquot portions were collected in small phials, cooled in ice, and scanned when convenient. Spectra were measured with reference cells filled with matching phosphine solutions when appropriate.

TABLE 2

Solubility of carbon monoxide in decalin

t/°C	Ostwald coefficient, L	10^4X_2	$10^4(X_2)_1$	10^3[CO]/M
20·0	0·141	9·17	9·17	5·9
39·9	0·148	9·15	9·19	5·8
59·9	0·160	9·35	9·49	5·7
75·6	0·162	9·03	9·30	5·5

Gas Solubility.—The solubility of carbon monoxide in decalin was measured by the method of Morrison and Billett.[6] Table 2 shows the values of the Ostwald coefficient L, the mole fraction of dissolved gas X_2, and the mole fraction of dissolved gas $(X_2)_1$ for a gas pressure above the solution of 1 atm.[7] The molar solubility at any temperature and for any partial pressure of gas was calculated by assuming Henry's law and using the average of measured values of $(X_2)_1$. This was multiplied by $(1 - P_d)x$, where x is the fraction of carbon monoxide in the gas mixture employed and P_d the vapour pressure of decalin at

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[4] R. Ball, M. J. Bennett, E. H. Brooks, W. A. G. Graham, J. Hoyano, and S. M. Illingworth, *Chem. Comm.*, 1970, 592.

[5] S. A. Fieldhouse, Ph.D. Thesis, University of Toronto, 1971, p. 84.

[6] T. J. Morrison and F. Billet, *J. Chem. Soc.*, 1948, 2033.

[7] E. Wilhelm and R. Battino, *Chem. Rev.*, 1973, **73**, 1.

that temperature.[8] Division by the appropriate molar volume of decalin [9] leads to the molar concentration of carbon monoxide. These values are probably accurate to better than ±5%.

Reactions.—(I) + CO $\rightleftharpoons$ (II). This reaction was followed at 70—100 °C by observing changing intensities of bands at 1 834 and 2 100 cm^{-1} due to complexes (I) and (II) respectively. Reaction of complex (II) under an atmosphere of argon gave 100% yields of (I) but reactions of either of them under carbon monoxide led to equilibrium mixtures. The approach to equilibrium gave first-order rate plots linear for *ca.* three half-lives irrespective of the starting complex. Data (Table 3) at 90 °C show that the observed rate constants are given by the rate law $k_{obs} = k_{CO}[CO] + k_{-CO}$. The constant k_{-CO} can be obtained directly, and values of k_{CO} can therefore be obtained from $(k_{obs} - k_{-CO})/[CO]$. It was also found that values of k_{-CO} obtained directly were very close to rate constants observed for reaction of complex (II) with triphenylphosphine (Table 6) and the latter values are therefore used to supplement the former. All the values were combined to derive activation parameters $\Delta H_{-CO}^{\ddagger}$ and $\Delta S_{-CO}^{\ddagger}$ by a least-squares procedure in which all rate constants were assumed to have the same percentage uncertainty. Equilibrium constants were calculated both from the ratios $k_{CO} : k_{-CO}$ and intensity ratios of the i.r. bands at 1 834 and 2 100 cm^{-1}. The agreement was generally very good. Values of ΔH^0 and ΔS^0 were obtained by least-squares analysis, each value of K being assumed to have the same percent uncertainty. Although this will not be true the assumption will result in an overestimate of the uncertainties which will do something to compensate for errors introduced into ΔH^0 and ΔS^0 by overweighting of less-precise data. The standard deviation of ±12% obtained for an individual measurement of the equilibrium constants seems quite good in the circumstances.

TABLE 3

Kinetic parameters for the reaction (I) + CO $\rightleftharpoons$ (II) in decalin. [Complex] = *ca.* 7 × 10^{-4}M

$\frac{t}{°C}$	$\frac{P_{CO}}{atm}$	$\frac{10^3[CO]}{M}$	$\frac{10^4 k_{obs}}{s^{-1}}$	$\frac{10^4 k_{-CO}}{s^{-1}}$	$\frac{10^2 k_{CO}\,^a}{l\,mol^{-1}\,s^{-1}}$	K/l mol^{-1} *b*	K/l mol^{-1} *c*
70·0	1·00	5·6	1·13 [d]	0·394 [e]	1·32	335	347
80·0	1·00	5·4	3·32 [d]	(1·47) [f]	3·40	231	180
				1·65 [e]	3·07	186	
80·0	0·00	0·0	1·47	1·47			
90·0	1·00	5·2	11·1	(6·60)	8·59	130	126
90·0	0·52	2·7	8·80	(6·60)	8·09	123	143
90·0	0·27	1·4	7·80	(6·60)	8·51	129	153
90·0	0·051	0·27	6·78	(6·60)	*ca.* 7	*ca.* 106	
90·0	0·00	0·00	6·60	6·60			
90·0	0·00	0·00	6·60	6·60			
100·0	0·00	0·00	27·2	27·2			

$\Delta H_{-CO}^{\ddagger} = 143{\cdot}5 \pm 2{\cdot}0$ kJ mol^{-1} ($34{\cdot}34 \pm 0{\cdot}48$ kcal mol^{-1}) [g]
$\Delta S_{-CO}^{\ddagger} = 88{\cdot}0 \pm 5{\cdot}6$ J K^{-1} mol^{-1} ($21{\cdot}0 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}) [g]
$\sigma(k_{obs}) = \pm 7{\cdot}2\%$ [g]
$\Delta H_{CO}^{\ddagger} = 92{\cdot}87 \pm 1{\cdot}67$ kJ mol^{-1} ($22{\cdot}22 \pm 0{\cdot}60$ kcal mol^{-1})
$\Delta S_{CO}^{\ddagger} = -11{\cdot}2 \pm 4{\cdot}7$ J K^{-1} mol^{-1} ($-2{\cdot}7 \pm 1{\cdot}8$ cal K^{-1} mol^{-1})
$\sigma(k_{obs}) = \pm 4{\cdot}7\%$.
$\Delta H^0 = -47{\cdot}47 \pm 4{\cdot}50$ kJ mol^{-1} ($-11{\cdot}34 \pm 1{\cdot}08$ kcal mol^{-1})
$\Delta S^0 = -90{\cdot}1 \pm 12{\cdot}6$ J K^{-1} mol^{-1} ($-21{\cdot}5 \pm 3{\cdot}0$ cal K^{-1} mol^{-1})
$\sigma(K) = \pm 11{\cdot}6\%$

[a] From $(k_{obs} - k_{-CO})/[CO]$. [b] From k_{CO}/k_{-CO}. [c] From [(II)]/[(I)][CO] at equilibrium. [d] Starting from complex (I); all other runs started from (II). [e] k_{-CO} Assumed equal to k_{PPh_3} (see Table 6). [f] Values in parentheses are taken from k_{obs} when P_{CO} = 0. [g] Values obtained by pooling k_{-CO} values with k_{obs} for reaction of PPh_3 with complex (II) (Table 6).

Complex (I) *with* PPh_3 *and* PBu_3. These reactions proceeded smoothly to completion at 20—50 °C and good first-order rate plots were obtained by monitoring the decreasing intensity of the band at 1 834 cm^{-1} due to complex (I). The rate constants (Table 4) obey the rate law $k_{obs} = k_1 + k_2[L]$ and values of k_1 and k_2 and their standard deviations were obtained by a weighted least-squares analysis in which each value of k_{obs} was assumed to have constant percentage uncertainty. Since the number of degrees of freedom at each temperature is small, and since deviations of k_{obs} from the corresponding calculated values did not show any systematic trends from group to group, all deviations were pooled to give a value of $\sigma(k_{obs})$ from 23 points of ±4·1%, after allowance for the 13 degrees of freedom. The standard deviations for k_1 and k_2 are based on this estimate of uncertainty of a single observation, and 95% confidence limits can therefore be obtained by doubling the standard deviations. For L = PPh_3 activation parameters were estimated from values of k_1 and k_2 by an appropriately weighted least-squares analysis.

When reactions were carried out under an atmosphere of carbon monoxide some were found to be retarded, compared with those under argon, the retardation being proportionately much greater at lower phosphine concentrations. The products of the reactions under argon were generally found to be mixtures of the monophosphine complex (IV; L = PPh_3) and the bisphosphine (III; L = PPh_3). The bis-complex must be a direct product of the reaction because reaction of the mono-complex with triphenylphosphine to form the bis-complex is relatively much slower (see below). At high phosphine concentrations, or under carbon monoxide, only the mono-complex was formed. This could then be converted quantitatively

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[8] J. Timmermans, 'Physico-chemical Constants of Pure Organic Compounds,' Elsevier, Amsterdam, 1965, vol. 2, pp. 170—173.

[9] W. F. Seyer and C. H. Davenport, *J. Amer. Chem. Soc.*, 1941, **63**, 2425.

into the bis-complex by further reaction at *ca.* 100 °C. In this way relative absorption coefficients of the mono-complex at 2 089 cm^{-1} and the bis-complex at 1 976 cm^{-1} were obtained and subsequently used to estimate the relative amounts of mono- and bis-complex present under conditions where mixtures were formed. The ratios of mono- to bis-complex in some product solutions are listed in Table 5 where they can be seen to correlate well with the ratio k_2[PPh$_3$] : k_1, each ratio probably having a precision of no better than ±10%. Thus, within experimental error and in the absence of carbon monoxide, the mono-complex is formed only by the second-order reaction whereas the first-order path leads only to the bis-complex. Under carbon monoxide the first-order path also leads only to the monophosphine complex.

TABLE 4

Kinetic parameters [a] for the reaction (I) + L $\longrightarrow$ (IV) + (III) in decalin (L = PPh$_3$ or PBu$_3$). [Complex] = *ca.* 7 × 10^{-4}M

t/°C	10^3[PPh$_3$]/M	10^5 k_{obs}/s^{-1}
19·6	22·8	4·22
	50·1	8·83
	98·0	14·4
	234	33·6
10^5k_1 = 1·131 ± 0·231 s^{-1}		
10^3k_2 = 1·402 ± 0·051 l mol^{-1} s^{-1}		
29·8	9·85	6·03
	52·0	21·1
	105	42·4
	220	85·0
10^5k_1 = 2·323 ± 0·291 s^{-1}		
10^3k_2 = 3·731 ± 0·109 l mol^{-1} s^{-1}		
39·8	3·92	11·8
	3·92 [b]	6·0
	7·10	15·4
	21·2	29·2
	44·8	54·1
	44·8 [b]	52·0
	71·5	75·6
10^5k_1 = 8·160 ± 0·450 s^{-1}		
10^3k_2 = 9·821 ± 0·292 l mol^{-1} s^{-1}		
50·0	3·90	37·2
	3·96	36·1
	3·96 [b]	13·9
	10·0	55·0
	10·0 [b]	33·5
	19·0	74·5
	30·0	105
	30·0 [b]	91·4
10^5k_1 = 26·68 ± 1·34 s^{-1}		
10^3k_2 = 26·08 ± 1·37 l mol^{-1} s^{-1}		
$\Delta H_1^\ddagger$ = 88·50 ± 3·53 kJ mol^{-1} (21·17 ± 0·84 kcal mol^{-1})		
$\Delta S_1^\ddagger$ = −40·2 ± 11·2 J K^{-1} mol^{-1} (−9·6 ± 2·7 cal K^{-1} mol^{-1})		
$\Delta H_2^\ddagger$ = 72·44 ± 1·38 kJ mol^{-1} (17·33 ± 0·33 kcal mol^{-1})		
$\Delta S_2^\ddagger$ = −51·92 ± 4·51 J K^{-1} mol^{-1} (−12·4 ± 1·1 cal K^{-1} mol^{-1})		

t/°C	10^3[PBu$_3$]/M	10^5k_{obs}/s^{-1}
29·8	12·4	13·8
	60·5	50·6
	120	101
	174	141
10^5k_1 = 4·21 ± 0·69 s^{-1}		
10^3k_2 = 7·74 ± 0·23 l mol^{-1} s^{-1}		

[a] All uncertainties are estimates of standard deviations based on a value of σ(k_{obs}) = ±4·1% obtained by pooling all the data. [b] Under 1 atm carbon monoxide.

TABLE 5

Relative yields of complexes (IV; L = PPh$_3$) and (III; L = PPh$_3$) from the reaction of triphenylphosphine with (I)

$\frac{t}{°C}$	$\frac{10^3[PPh_3]}{M}$	[(IV)]/[(III)] [a]	k_2[PPh$_3$] : k_1 [b]
50·0	3·90	0·35	0·38
	10·0	0·79	0·98
	19·0	1·70	1·85
	30·0	2·33	2·93
39·8	3·92	0·52	0·47

[a] Based on a ratio of 0·4 for absorption coefficients at 2 089 and 1 976 cm^{-1} for complexes (IV) and (III) respectively.

Complex (II) *with* PPh$_3$ *and* PBu$_3$. These were followed by measuring the decreasing intensity of the band at 2 100 cm^{-1}. The reactions went to completion under all conditions and gave good first-order rate plots. Data are reported in Table 6. The values of k_{obs} for the reaction with triphenylphosphine were independent of [PPh$_3$] and were also quite unaffected when the reactions were carried out under an atmosphere of carbon monoxide even when [PPh$_3$] was as low as 4 × 10^{-3}M. The reaction with tri-n-butylphosphine obeyed the rate law $k_{obs} = k_1 + k_2$[PBu$_3$] and values for k_1 and k_2 are also shown in Table 6, the value of k_1 being in excellent agreement with that obtained from the ring closure and triphenylphosphine reactions.

TABLE 6

Kinetic parameters [a] for reaction of complex (II) with PPh$_3$ and PBu$_3$ in decalin. [Complex] = *ca.* 7 × 10^{-4}M

t/°C	10^3[PPh$_3$]/M	10^5 k_{obs}/s^{-1}
70·0	4·35	3·83
	330	4·05
80·0	74·0	16·5
90·0	53·0	65·0
	92·0	65·7
100·0	3·74	231
	3·74 [b]	226
	80·0	234
90·0	12·4 [c]	68·0
	29·4 [c]	71·6
	70·0 [c]	76·8
	166 [c]	97·6
10^4 k_1 = 6·54 ± 0·15 s^{-1} [d]		
10^3 k_2 = 1·89 ± 0·20 l mol^{-1} s^{-1} [d]		

[a] Activation parameters, given in Table 3, from pooled results of the reaction with PPh$_3$ and that forming complex (I). [b] Under 1 atm carbon monoxide. [c] PBu$_3$. [d] Uncertainty assumes σ(k_{obs}) = ±7·2% (see Table 3 and text).

The reaction with triphenylphosphine was found to yield mixtures of the mono- and bis-phosphine complexes (IV; L = PPh$_3$) and (III; L = PPh$_3$) in ratios that closely resembled those found after reaction of complex (I) under comparable conditions, though at lower temperatures. Thus at 100 °C and [PPh$_3$] = 3·74 × 10^{-3}M the product was almost entirely the bis-complex, unless reaction was carried out under an atmosphere of carbon monoxide when only the mono-complex was formed directly. (Some bis-complex was formed by the subsequent substitution reaction with phosphine that occurs at an observable rate at this temperature.) Similarly, at 70 °C and $[PPh_3] = 4{\cdot}35 \times 10^{-3}$M only the bis-complex was observed whereas for $[PPh_3] = 0{\cdot}33$M the directly formed product was only the mono-complex.

Complex (IV; L = PPh_3 *and* PBu_3) *with* L. Solutions of the monophosphine complexes were generated by reaction of a phosphine with (I) under conditions such that the bis-complex was not formed (see above); the conditions were then adjusted so that further substitution occurred. The reactions were followed by measuring the decreasing intensity of the bands at 2 089 cm^{-1} (L = PPh_3) or 2 084 cm^{-1} (L = PBu_3) and went to completion under all conditions used. Values of k_{obs} are shown in Table 7.

TABLE 7

Kinetic parameters for the reaction (IV) + L $\longrightarrow$ (III) + CO in decalin (L = PPh_3 and PBu_3). [Complex] = *ca.* 7×10^{-4}M

t/°C	$10^3[PPh_3]$/M	$10^5k_{obs}/s^{-1}$
90·0	50·1	17·2
	98·0	16·8
100·0	52·0	59·1
	114	58·7
110·0	105	204
	220	204
120·0	3·96	610
	3·96	363 [a]
	7·10	488 [a]
	10·0	550 [a]
	15·0	574 [a]
	21·2	628
	44·8	635 [a]
	100	625
	234	630

$\Delta H^{\ddagger} = 139{\cdot}9 \pm 0{\cdot}67$ kJ mol^{-1} ($33{\cdot}47 \pm 0{\cdot}16$ kcal mol^{-1})

$\Delta S^{\ddagger} = 66{\cdot}8 \pm 1{\cdot}8$ J K^{-1} mol^{-1} ($16{\cdot}0 \pm 0{\cdot}4$ cal K^{-1} mol^{-1})

$\sigma(k_{obs}) = \pm 2{\cdot}1\%$

t/°C	$10^3[PPh_3]$/M	$10^5k_{obs}/s^{-1}$
90	12·4 [b]	31·4
	53·0 [b]	71·8
	60·5 [b]	68·2
	120 [b]	148
	174 [b]	228
	296 [b]	444

[a] Under 1 atm carbon monoxide. [b] PBu_3.

When L = PPh_3 values of k_{obs} were independent of $[PPh_3]$ but the reaction was increasingly retarded by carbon monoxide as $[PPh_3]$ was lowered. When L = PBu_3 the rate increased with $[PBu_3]$, the dependence being greater than first order. The initial gradient of a plot of k_{obs} against $[PBu_3]$ corresponded to a second-order rate constant of $\lesssim 10^{-2}$ l mol s^{-1} at 90 °C, and the intercept at $[PBu_3] = 0$ to $k_1 \simeq 2 \times 10^{-4}$ s^{-1}. As the rate became significantly greater than the first-order dependence on $[PBu_3]$ would predict, new bands at 1 910 and 1 965 cm^{-1} were clearly apparent in the i.r. spectra. Fieldhouse [10] has found that, at high concentrations of ligand, the Ph_2Ge group can be displaced from these complexes by phosphines and phosphites with the formation of complex mixtures of substituted cobalt carbonyls and other, unidentified, products.

DISCUSSION

The results can best be discussed in terms of the Scheme which outlines the course of the reactions between the various complexes and carbon monoxide or triphenylphosphine.

Reactions.—(II) $\rightleftharpoons$ (I) + CO. The reverse reaction follows the rate law $k_{obs} = k_{CO}[CO]$ and it could therefore be a concerted bimolecular reaction. An alternative is a two-step mechanism involving initial formation of the co-ordinatively unsaturated ring-opened intermediate $[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3]$ which undergoes ring closure to reform the reactant much more rapidly than attack by carbon monoxide to form complex (II). The ring-closure reaction of complex (II) can likewise proceed by either the concerted or two-step mechanism. This reaction is governed by a positive activation entropy of +88 J K^{-1} mol^{-1} that falls within the range characteristic of a CO-dissociative process.[11,12] Although $\Delta S_{-CO}^{\ddagger} \simeq \Delta S_{-CO}^{0}$ this does not necessarily imply that the transition state resembles at all closely the products of reaction. The complete release of a carbon monoxide molecule from the transition state containing a stretched Co $\cdots$ CO bond would be accompanied by an increase of 172 J K^{-1} mol^{-1} in entropy (*i.e.* the standard entropy of carbon monoxide at a standard state of 1M [13]) and a decrease in entropy, on subsequent ring closure, of equal magnitude is quite reasonable. The two-step reaction involving the intermediate $(\mu\text{-}Ph_2Ge)\{Co(CO)_4\}\{Co(CO)_3\}$ is, therefore, quite plausible. Correcting the value of ΔS_{-CO}^{0} for the standard entropy of the carbon monoxide released provides a value of −82 J K^{-1} mol^{-1} for the difference in entropy between the open complex (II) and the cluster (I).

Complex (II) *with* PPh_3 *and* PBu_3. The close agreement of the rates of reaction with triphenylphosphine with those of ring closure to form complex (I), and the nature of the products under various conditions, strongly suggest that the reaction proceeds by rate-determining formation of (I), followed by rapid reaction of this complex with triphenylphosphine. The absence of any inhibition by carbon monoxide of the sort usually observed with the CO-dissociative mechanism does not invalidate the argument for a CO-dissociative two-step reaction *via* $(\mu\text{-}Ph_2Ge)\{Co(CO)_4\}\{Co(CO)_3\}$, since it is implicit in this mechanism that the intermediate undergoes ring closure much more rapidly than attack by carbon monoxide even at the highest attainable concentrations of the latter. For similar reasons the fact that no complex (IV; L = PPh_3) is observed as the product of reaction of (II) with 4×10^{-3}M-triphenylphosphine is also not inconsistent with this mechanism. The formation of the monophosphine complex at higher concentrations of triphenylphosphine is known to occur *via* the second-order reaction of triphenylphosphine with (I) and this too can be occurring *via* $(\mu\text{-}Ph_2Ge)\{Co(CO)_4\}$-

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[10] Ref. 5, pp. 166—169.

[11] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn.

[12] R. J. Angelici, *Co-ordination Chem. Rev.*, 1968, **3**, 173.

[13] National Bureau of Standards, U.S. G.P.O., Washington, D.C., 1952, Circular 500.

$\{Co(CO)_3\}$ in a two-step mechanism (see below), the concentration of triphenylphosphine now being great enough for its attack on the intermediate to compete with ring closure. The second-order reaction with tributylphosphine probably involves direct nucleophilic attack at a cobalt atom.

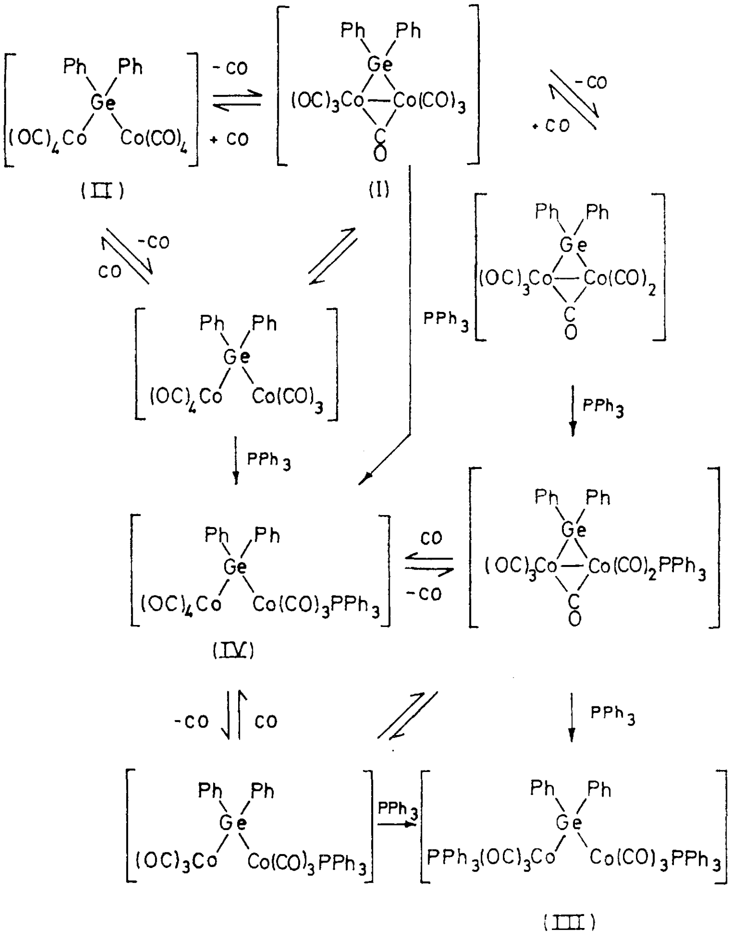
Complex (I) *with* PPh_3 *and* PBu_3. The data suggest that the second-order reactions proceed by the two-step mechanism involving $(\mu\text{-}Ph_2Ge)\{Co(CO)_4\}\{Co(CO)_3\}$ as an intermediate. This would not be expected to show much discrimination in its reactions with a ligand and $k_2(PBu_3)/k_2(PPh_3)$ is only *ca.* 2 at 30 °C while $k_2(PPh_3)/k_2(CO)$ is only *ca.* 20 at 30 °C. This discrimination is much less than would be expected for a concerted process.[11,12,14]

The nature of the products from the first-order path, and the retardation of the rates by carbon monoxide, are consistent with the CO-dissociative substitution path indicated in the Scheme, the substituted cluster complex $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ then undergoing rapid ring-opening reaction with triphenylphosphine or carbon monoxide. Although the value of -40 J K^{-1} mol^{-1} for the entropy of activation of the first-order path is not characteristic of a CO-dissociative reaction[11,12] of mononuclear carbonyl complexes, the contribution to the activation entropy of changes in bonding within the cluster as carbon monoxide dissociates is an unknown factor and the negative value of the activation entropy cannot, therefore, be taken as strong evidence against a dissociative mechanism. Ellgen has also obtained a negative value of $\Delta S^{\ddagger}$ for dissociation of carbon monoxide from cobalt octacarbonyl.[15] The inhibition of the first-order path by carbon monoxide is positive evidence in favour of a dissociative mechanism. For a reaction proceeding by both CO-dissociative and second-order paths the ratio, $k_{CO} : k_{PPh_3}$, of rate constants for bimolecular attack at the co-ordinatively unsaturated intermediate in the dissociative path, is given by equation (1), where k_{-CO}

$$k_{CO}/k_{PPh_3} = [L][k_{obs}(Ar) - k_{obs}(CO)]/[CO]\{k_{-CO} - [k_{obs}(Ar) - k_{obs}(CO)]\} \quad (1)$$

is the limiting rate of the dissociative path and $k_{obs}(Ar)$ and $k_{obs}(CO)$ are observed rate constants under atmospheres of argon and carbon monoxide, respectively, at the same concentrations of phosphine. The data in Table 4 lead to approximate values of 2 and 5 : 1 at 30 and 50 °C, respectively, for this ratio. Values for ratios such as these are rather rare, but these are close to those found for k_{CO}/k_{PBu_3} in dissociative substitution reactions of the complexes $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ with PBu_3 (L = CO or PBu_3).[16]

The ring-opening reactions of the complex $[(OC)_3CO(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ can also proceed either by concerted or two-step mechanisms. Whichever they are, replacement of a carbonyl ligand in complex (I) by a phosphine evidently makes the ring-opening process very much more rapid. The reaction of carbon monoxide with complex (I) is slow at 100 °C; but that with $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ must be quite fast even at 20 °C. The fact that the mono-phosphine complex is the only product formed at 40 °C when the reaction is carried out under 1 atm carbon monoxide ($[CO] = ca.\ 5 \times 10^{-3}$M), even when $[PPh_3] = 45 \times 10^{-3}$M, suggests that carbon monoxide must compete at least 10^2 times more effectively than triphenylphosphine for $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ or $(\mu\text{-}Ph_2Ge)\{Co(CO)_3PPh_3\}\{Co(CO)_3\}$. This ratio shows a high absolute discrimination in favour of carbon monoxide, and the effect of replacing a carbonyl ligand in complex (I) by triphenylphosphine changes the competition ratio by $\gtrsim 10^3$. This is a strong indication that the reactions of the complex $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ with carbon monoxide and triphenylphosphine are concerted, $(\mu\text{-}Ph_2Ge)\{Co(CO)_3PPh_3\}\{Co(CO)_3\}$ being most unlikely to show this degree of discrimination. For example, competition between carbon monoxide and tributylphosphine for the co-ordinatively unsaturated intermediates $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_2]$ is almost unaffected by whether L = CO or PBu_3, whereas the



SCHEME

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[14] A. J. Poë and M. V. Twigg, *J. Organometallic Chem.*, 1973, **50**, C39.

[15] P. C. Ellgen, *Inorg. Chem.*, 1972, **11**, 691.

second-order rate constant for attack by tributylphosphine on $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ is very much smaller when $L = PBu_3$ rather than CO.[16]

Complex (IV; $L = PPh_3$ *and* PBu_3) *with* L. When $L = PPh_3$ the data are consistent either with a straightforward CO-dissociative mechanism, with competition between carbon monoxide and phosphine for the co-ordinatively unsaturated intermediate, or with concerted ring closure, with loss of carbon monoxide, to form $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ which is then attacked directly by triphenylphosphine or by carbon monoxide if it is present. If $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ is regarded as a reactive intermediate under these conditions, both mechanisms would obey the rate law given in equation (2) so that a plot of $1/k_{obs}(CO)$ against $1/[PPh_3]$ should give a straight line

$$k_{obs}(CO) = (k_{-CO}k_{PPh_3}[PPh_3]/k_{CO}[CO])/\{1 + (k_{PPh_3}[PPh_3]/k_{CO}[CO])\} \quad (2)$$

of intercept $1/k_{-CO}$ and gradient $k_{CO}[CO]/k_{-CO}k_{PPh_3}$. A good straight line was indeed obtained from the data at 120 °C (Table 7); k_{-CO} was found to be $6{\cdot}7 \times 10^{-3}\ s^{-1}$, in excellent agreement with the value of $k_{obs}(Ar)$, and $k_{CO}/k_{PPh_3} = 0{\cdot}6$. This competition ratio is very different from the value of $\gtrsim 10^2$ deduced above for concerted reactions with the complex $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ at 40 °C and it is most improbable that the different temperatures could account for this. It is probable that the CO-dissociative mechanism occurs in preference to the two successive concerted reactions, and the relatively high value of $\Delta H^\ddagger$ and the positive $\Delta S^\ddagger$ for this reaction are in perfect accord with this.

From the above discussion it would seem reasonable to conclude that, of those reactions in the Scheme that are shown as having possible alternative paths, those paths that involve co-ordinatively unsaturated intermediates are followed for all the reactions, except those of $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_2PPh_3]$ with carbon monoxide and triphenylphosphine. It is also possible that the reactions can proceed by both paths, relative contributions of each depending on the particular complex and ligand involved.

For the reaction of complex (IV; $L = PBu_3$) with tributylphosphine there is at least one path dependent on $[PBu_3]$ in addition to the CO-dissociative one, but interference from a side reaction (probably associated with elimination of the Ph_2Ge group [10]) prevents straightforward quantitative study. Reactions of Lewis bases with metal carbonyl complexes containing Group IV ligands of this type are frequently complicated by such processes [10,17] and co-ordination of the base to the Group IV atom seems a probable explanation.[17] The simple second-order substitution, however, is more likely to involve nucleophilic attack at the transition metal. The approximate value of the second-order rate constant for substitution at 90 °C, found from the initial gradient of a plot of k_{obs} against $[PBu_3]$, is about five times greater than that for the corresponding reaction of complex (II), showing that steric effects of substitution in these complexes are much smaller than those in similar reactions of $[L(OC)_2Co(\mu\text{-}C_2Ph_2)Co(CO)_3]$ ($L = CO$ or PBu_3).[16] This is in accordance with the more-open structures of complexes (II) and (IV; $L = PBu_3$). The Group IV ligand atoms appear to enhance the tendency towards bimolecular substitution which has also been shown to occur in the complexes $[Ph_3MMn(CO)_5]$ (M = Ge and Sn).[18] The value of the first-order rate constants for reactions of complexes (II) and (IV; $L = PPh_3$ or PBu_3) are very similar so that substituents on one cobalt atom have very little effect on the CO-dissociative reaction at the other.

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[3/2149 *Received, 22nd October*, 1973]

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