Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part VII.[1] Reaction of Alkynes with μ-Carbonyl-μ-diphenylgermanio-bis(tricarbonylcobalt)(*Co–Co*)

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Alkynes [C_2Ph_2, MeC_2Ph, PhC_2H, and $C_2(CO_2Et)_2$] displace the bridging $GePh_2$ group from $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$, (I), to form the well known complexes $[(OC)_3\overline{Co(\mu\text{-}alkyne)Co}(CO)_3]$ together with $(GePh_2)_n$ (n = 4—7). The kinetics of reaction of complex (I) with diphenylacetylene in decalin have been studied over a range of temperature. The rate of reaction is first order in [Complex] and [C_2Ph_2] and the reaction is greatly retarded by carbon monoxide. The results are consistent with a reaction mechanism that involves initial reversible ring opening to form $[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$,† a process that is also involved in reactions of complex (I) with carbon monoxide and triphenyl- and tributyl-phosphine. A mechanism involving intermediates with terminally co-ordinated $GePh_2$ groups cannot be conclusively ruled out but is considered to be less probable.

THE complex $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$, (I), is believed to be structurally derived from the carbonyl-bridged form of cobalt octacarbonyl by replacement of one bridging carbonyl ligand by a diphenylgermanio-bridge.[2] However, the question of whether $GePh_2$ is capable of acting as a unidentate carbene-like ligand, either in a reactive intermediate or in a stable complex, is still an open one. The fluxional behaviour[3] of the complex $[Co_2(CO)_6(GeMe_2)_2]$ can be readily explained[4] in terms of such an intermediate although Adams and Cotton[3] prefer an alternative mechanism. Curtis and Job[5] suggested that terminal $GeMe_2$ groups may be present in the complexes $[Mn_2(CO)_9(GeMe_2)]$ and $[Mn_2(CO)_8(GeMe_2)_2]$ although more recently they favour bridging dimethylgermanio-structures.[6] Several kinetic studies have been made[7–10] of rates of reaction of alkynes with cobalt carbonyls to form alkyne-bridged complexes. Kinetic evidence for accumulation of intermediates such as $[Co_2(CO)_7(alkyne)]$ has been adduced.[7–9] In these cases the cobalt carbonyls exist, or can easily exist, in the non-bridged form with unsupported Co–Co bonds. Reaction of alkynes with complex (I) has been shown[11] to result in smooth displacement of a carbonyl ligand and the bridging $GePh_2$ group, and intermediacy of complexes with terminal $GePh_2$ groups was suggested. We now report details of these reactions together with results of a kinetic study of the reaction of diphenylacetylene with the complex. Kinetics of reactions of complex (I) with carbon monoxide and triphenyl- and tri-n-butylphosphine have been thoroughly studied[1] and interpreted without having to invoke the existence of terminally bonded Ph_2Ge groups.

EXPERIMENTAL

The complex $[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$, (I), was prepared and characterised as described previously[2] and was stored in the dark under a nitrogen atmosphere. Diphenylacetylene (Baker Chemicals) and the other alkynes were used as received. Analysed mixtures of carbon monoxide and nitrogen ($\pm 2\%$) were obtained from Matheson of Canada. Argon (99·998%) was obtained from Union Carbide of Canada, Ltd. Decalin (Baker Analysed Reagent) was stored over molecular sieves.

Reaction of Complex (I) *with Diphenylacetylene.*—All reactions were effected under an atmosphere of nitrogen and with dried and deoxygenated solvents. Diphenylacetylene (0·18 g, 1 mmol) was added to a solution of complex (I) (0·54 g, 1 mmol) in hexane (20 cm^3) and the solution was stirred at room temperature for 10 days. The yellow precipitate that formed was filtered off and the supernatant solution was passed through an alumina column. Elution with hexane gave a red fraction which yielded 0·39 g (79%) of the known[12] complex $[(OC)_3\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_3]$.

Similar results were obtained with phenylacetylene (reaction time 12 h), phenylmethylacetylene, and diethyl acetylenedicarboxylate. The yellow solid product from the reaction with phenylmethylacetylene was washed with hexane and dried. It was soluble in benzene and toluene but insoluble in hexane. The ^1H n.m.r. spectrum in hexadeuteriobenzene showed only aromatic protons, and the i.r. spectrum in Nujol and hexachlorobutadiene mulls showed a large number of bands characteristic of a Ph–Ge system but not of any other functional groups, *viz.* 3 060, 3 045, 3 021, 2 980, 1 602, 1 560, 1 448, 1 431, 1 262, 1 183, 1 156, 1 099, 1 092, 1 026, 997, and 703 cm^{-1}. A complete mass spectrum (JEOLCO 01-SC high-resolution spectrometer) could not be obtained but, below *m*/*e* 600,

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† This structural formula could be written as $\mu\text{-}Ph_2Ge\{Co(CO)_4\}\{Co(CO)_3\}$ as in Part VI.[1] However, the convention has been adopted here of using the formulation $\overline{Co(\mu\text{-}X)Co}$ when X bridges a Co–Co bond, and Co(μ-X)Co when X bridges two cobalt atoms that are not bonded to each other.

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

[9] F. Ungváry and L. Markó, *Chem. Ber.*, 1972, **105**, 2457.

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

[11] S. A. Fieldhouse, Ph.D. Thesis, University of Toronto, 1971.

[12] G. Peyronel, A. Ragni, and E. F. Trogu, *Gazzetta*, 1962, **92**, 738.

the spectrum closely resembled those reported[13] for $(GePh_2)_n$ (n = 4—7). The large m.p. range for the sample (137—163 °C) showed that the product was a mixture of the possible cyclopolygermanes but no attempt was made at separation (Found:* C, 63·1; H, 4·4. Calc. for $C_{12}H_{10}Ge$: C, 63·5; H, 4·4%).

Kinetic Procedures.—Solutions were prepared and deoxygenated, kinetic runs carried out, and concentrations of carbon monoxide derived, as described previously.[1,10] Most reactions were performed in a Schlenk tube under mixed CO–N_2 atmospheres but in some cases a steady flow of argon was maintained through the solutions, the flow rate being monitored in an oil bubbler. Samples were ejected by temporarily closing the exit to build up pressure before inserting a stainless-steel sample-ejection tube. Samples were ejected directly into i.r. cells and spectra measured immediately in the C–O stretching region by means of a Perkin-Elmer 257 spectrophotometer, reference cells being filled with solutions of diphenylacetylene as appropriate. I.r. spectra of the product and reactant complexes differed appreciably only in a band at 1 839 cm^{-1} characteristic[2] of the bridging carbonyl ligand in (I) so that only the rate of disappearance of this complex was observed.

RESULTS

Reactions with Diphenylacetylene.—(a) *Under carbon monoxide.* Under 1 atm carbon monoxide, reaction in the presence of 0·1M-diphenylacetylene did not lead to any acetylene-containing product, formation of the complex $[(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_4]$ predominating. The rate of formation of this complex is known[1] to be dependent on the concentration of carbon monoxide and, provided the partial pressure was kept below 0·3 atm, this product was not observed. Reaction under a static atmosphere of argon gave curved first-order rate plots, the gradients decreasing appreciably after less than one half-life. This suggested that the reaction was inhibited by carbon monoxide, so reactions were generally followed under a known partial pressure of carbon monoxide below 0·3 atm when quite good first-order rate plots were obtained. Reactions went to completion and a fine yellow precipitate was observed in the bottom of the reaction vessels after each run. Observed rate constants are reported in the Table. Plots of k_{obs} against $[C_2Ph_2]$ at constant [CO] were linear and passed through the origin. An analysis of the data by the method of pooled variances[14] gave a standard deviation of ±7·2% for an individual determination of k_{obs} if it was assumed that the deviation is independent of temperature and $[C_2Ph_2]$. A plot of $[C_2Ph_2]/k_{obs}$ against [CO] was linear with a very small, but possibly significant, intercept. A weighted least-squares analysis led to a gradient of $(2·73 \pm 0·28) \times 10^6$ s and an intercept of 47 ± 92 mol l^{-1} s. The inverse of the intercept should correspond to the rate constant for reaction in the absence of carbon monoxide and the data indicate that this can be said to be greater than $5·3 \times 10^{-3}$ l mol^{-1} s^{-1} at 80 °C with 95% confidence.

(b) *Under bubbling argon.* Some reactions were followed with argon bubbling through the solutions at an approximately constant rate. Reaction was much faster under these conditions and the kinetics were followed at a lower temperature. The observed first-order rate plots were linear and rate constants shown in the Table are again proportional to $[C_2Ph_2]$ above *ca.* 0·4M, a plot of k_{obs} against $[C_2Ph_2]$ passing through the origin. At lower concentrations reactions were faster than expected and when $[C_2Ph_2] = 0$ complex (I) reacted at a first-order rate that decreased with time but with an initial value of k_{obs} = *ca.* $1·3 \times 10^{-4}$ s^{-1}. When $[C_2Ph_2] \lesssim 0·5$M new bands appeared in the i.r. spectrum at 2 062 and 1 970 cm^{-1}. In the absence of diphenylacetylene these bands grew over the first 25% reaction and then decayed.

Kinetic data for reaction of complex (I) (7×10^{-4}M) with diphenylacetylene in decalin

t/°C	10^5[CO]/M	$10^3[C_2Ph_2]$/M	10^5k_{obs}/s^{-1}	$10^8(k_{obs}[CO]/[C_2Ph_2])$/s^{-1}
60·0	28·8	439	9·90	6·49
		873	21·7	7·16
70·1	28·4	308	12·9	11·9
		601	26·1	12·3
		877	37·6	12·2
80·0	27·7	100	11·8	32·7
		310	38·0	34·0
		580	80·5	38·4
		880	115	36·2
	83·8	880	35·0	33·3
	146	880	23·0	38·2
90·0	27·0	100	25·2	68·0
		159	37·1	63·0
		171	38·4	60·6
		304	80·1	71·1
50·0	*a*	0	*ca.* 13	
		21·0	30·8	
		425	66·0	155 [b]
		505	77·0	152 [b]
		569	88·4	155 [b]

[a] Carbon monoxide removed with bubbling argon. [b] $10^5(k_{obs}/[C_2Ph_2])$/l mol^{-1} s^{-1}.

DISCUSSION

The reactions studied here show that a carbonyl ligand and a bridging Ph_2Ge group can be smoothly displaced from the complex $[(OC)_3Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$, (I), by alkynes in the same way that two carbonyl ligands are displaced from cobalt octacarbonyl. The kinetic behaviour under a carbon monoxide atmosphere can be considered in the light of the mechanistic scheme proposed for reactions of complex (I) with carbon monoxide and triphenyl- and tributyl-phosphine.[1] The phosphines react in part by a path that is inhibited by carbon monoxide and that has been concluded to be a CO-dissociative process. This cannot be the major path for reaction with diphenylacetylene since rates of reaction under bubbling argon at 50 °C and at higher $[C_2Ph_2]$ exceed the limiting rate of the dissociative process. Complex (I) also reacts with carbon monoxide or the phosphines (L) by a path first order in the concentration of the entering ligand, the products being the ring-opened complexes $[(OC)_3LCo(\mu\text{-}GePh_2)Co(CO)_4]$. This reaction is believed to proceed by way of a very

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* Microanalysis was carried out by Huffman Laboratories, Inc., Wheatridge, Colorado 80033, U.S.A.

[13] K. Kuhlein and W. P. Neumann, *J. Organometallic Chem.*, 1968, **14**, 317 and refs. therein.

[14] J. Mandel, ' The Statistical Analysis of Experimental Data,' Interscience, New York, 1964, pp. 65—68.

easily reversed ring-opening process that forms $[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$, this co-ordinatively unsaturated intermediate then being attacked by the incoming ligand to form the fully co-ordinated product. Reaction with alkynes could also go *via* this sequence of reactions, followed by an additional reversible stage involving loss of carbon monoxide before final formation of product, as shown in equations (1)—(4).

$$[(OC)_3\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3] \rightleftharpoons [(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4] \quad (1)$$

$$[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4] + C_2Ph_2 \rightleftharpoons [(OC)_3(C_2Ph_2)Co(\mu\text{-}GePh_2)Co(CO)_4] \quad (2)$$

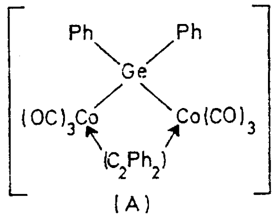
$$[(OC)_3(C_2Ph_2)Co(\mu\text{-}GePh_2)Co(CO)_4] \rightleftharpoons [(OC)_3(C_2Ph_2)Co(\mu\text{-}GePh_2)Co(CO)_3] + CO \quad (3)$$

$$[(OC)_3(C_2Ph_2)Co(\mu\text{-}GePh_2)Co(CO)_3] \longrightarrow [(OC)_3\overline{Co(\mu\text{-}C_2Ph_2)Co}(CO)_3] + GePh_2 \quad (4)$$

A steady-state treatment of the above mechanism leads to equation (5). Provided that $k_2k_3k_4[C_2Ph_2]$

$$k_{obs} = k_1k_2k_3k_4[C_2Ph_2]/\{k_{-1}(k_{-2} + k_3)k_4 + k_{-1}k_{-2}k_{-3}[CO] + k_2k_3k_4[C_2Ph_2]\} \quad (5)$$

is negligible compared with $k_{-1}(k_{-2} + k_3)k_4 + k_{-1}k_{-2}k_{-3}[CO]$ this rate equation is in accord with our results. The value $k_{obs}/[C_2Ph_2] \geqslant 5 \times 10^{-3}$ l mol^{-1} s^{-1} estimated for $[CO] = 0$ at 80 °C corresponds to $k_1(k_2/k_{-1})k_3/(k_{-2} + k_3)$. Since $k_3/(k_{-2} + k_3)$ cannot exceed unity, $k_1(k_2/k_{-1})$ must be $>5 \times 10^{-3}$ l mol^{-1} s^{-1}. For reaction with carbon monoxide[1] $k_1(k_2/k_{-1}) = 30 \times 10^{-3}$ l mol^{-1} s^{-1} so that diphenylacetylene cannot be much less nucleophilic than carbon monoxide towards the complex $[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$. On the other hand it is very unlikely to be more nucleophilic than triphenylphosphine for which $k_1(k_2/k_{-1})$ is 500×10^{-3} l mol^{-1} s^{-1}. This implies that k_3 must be $\geqslant 10^{-2}k_{-2}$, *i.e.* the rate of loss of carbon monoxide from the complex $[(OC)_3(C_2Ph_2)Co(\mu\text{-}GePh_2)Co(CO)_4]$ is not less than 1% of the rate of loss of diphenylacetylene. In order for steady-state conditions to apply, the absolute values of k_3 and k_{-2} must both be quite large and a high value for k_3 is surprising in view of the very slow dissociation of carbon monoxide from the complexes $[(OC)_3LCo(\mu\text{-}GePh_2)Co(CO)_4]$ (L = CO, PPh_3, or PBu_3).[1] This would seem to imply that diphenylacetylene must transmit an unusually large labilising effect through the germanium atom. However, since diphenylacetylene is a very strong bridging ligand in such systems, one could envisage (3) to be rapid intramolecular S_N2 displacement of carbon monoxide that competes moderately successfully with loss of the alkyne in the reverse of step (2). The product of step (3) would have the structure (A), in which C_2Ph_2 is bound to the cobalt atoms through its two orthogonal π-electron systems, and the bridging $GePh_2$ group would be lost in the final step and replaced by a Co–Co bond. Steps (2) and (3) could be combined into one reversible concerted process with some slight simplification of the rate equation but without changing its form.



(A)

Results when argon is bubbled through reacting solutions are also consistent with this mechanism. At higher values of $[C_2Ph_2]$ the constancy of $k_{obs}/[C_2Ph_2]$ implies that $k_2k_3 \ll k_{-1}(k_{-2} + k_3)$ and $k_{obs}/[C_2Ph_2] = k_1(k_2/k_{-1})k_3/(k_{-2} + k_3)$, provided that bubbling argon reduces [CO] essentially to zero. Thus, at 50 °C, $k_1(k_2/k_{-1}) > 1{\cdot}5 \times 10^{-3}$ l mol^{-1} s^{-1} as compared with 2×10^{-3} l mol^{-1} s^{-1} when carbon monoxide is attacking the complex $[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$.[1] Assuming, as before, that k_2 for attack by diphenylacetylene must be less than that for attack by triphenylphosphine, we find $k_3 \geqslant 5 \times 10^{-2}k_{-2}$. These limiting values for the relative rate constants are quite close to those found at 80 °C from reactions under a carbon monoxide atmosphere and the two sets of data are, therefore, quite compatible.

Results at low or zero values of $[C_2Ph_2]$ are less easy to understand. The new product does not have an i.r. spectrum characteristic of the complexes $Co_4(CO)_{12}$[15] or $Co_6(CO)_{16}$[16] and it is probably another $GePh_2$-containing species. The decreasing yield of this product as $[C_2Ph_2]$ increases might have been explained by reaction of the alkyne with the co-ordinatively unsaturated complex $[(OC)_2\overline{Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co}(CO)_3]$ were it not for the fact that the rate equation at high $[C_2Ph_2]$ does not include a term characteristic of the CO-dissociative path. At $[CO] = 2{\cdot}7 \times 10^{-4}$—$2{\cdot}9 \times 10^{-4}$M the rate equation is closely approximated by $k_{obs}[CO]/[C_2Ph_2] = k_1k_2k_3k_4/k_{-1}k_{-2}k_{-3}$. Least-squares analysis of the temperature dependence of $k_{obs}[CO]/[C_2Ph_2]$ leads to $\Delta H^‡ = 73{\cdot}2 \pm 2{\cdot}8$ kJ mol^{-1}, $\Delta S^‡ = -163 \pm 8$ J K^{-1} mol^{-1}, and $\sigma(k_{obs}) = \pm 10\%$. The rate constants at 70 °C are 30% below that calculated from these parameters. We assume this to have been caused by an unexplained systematic error and so have not included them in the computation. Inclusion gives parameters that have larger uncertainties but that do not differ significantly from the ones above.

The very negative value of $\Delta S^‡$ for formation of free carbon monoxide and the transition state in step (4) from complex (I) and diphenylacetylene can be understood in terms of the highly structured nature of (A). Most of the data can therefore be explained quite satisfactorily in terms of a mechanism closely related to

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[15] G. Bor, *Spectrochim. Acta*, 1963, **19**, 1209.

[16] P. Chini, *Chem. Comm.*, 1967, 440.

one already proposed for reactions of this complex.[1] However, an alternative mechanism that involves intermediates with terminal $GePh_2$ groups [equations (6)—(9)] should also be considered. Step (6) is assumed to be a rapidly set-up equilibrium lying well to the left-hand side and the rate equation is shown in (10). There is no change in the form of the rate equation

$$[(OC)_3Co(\mu\text{-}CO)(\mu\text{-}GePh_2)Co(CO)_3] \rightleftharpoons [(OC)_4Co\text{-}Co(CO)_3(GePh_2)] \quad (6)$$

$$[(OC)_4Co\text{-}Co(CO)_3(GePh_2)] \rightleftharpoons CO + [(OC)_3Co\text{-}Co(CO)_3(GePh_2)] \quad (7)$$

$$[(OC)_3Co\text{-}Co(CO)_3(GePh_2)] + C_2Ph_2 \rightleftharpoons [(C_2Ph_2)(OC)_3Co\text{-}Co(CO)_3(GePh_2)] \quad (8)$$

$$[(C_2Ph_2)(OC)_3Co\text{-}Co(CO)_3(GePh_2)] \longrightarrow [(OC)_3Co(\mu\text{-}C_2Ph_2)Co(CO)_3] + GePh_2 \quad (9)$$

$$k_{obs} = K_6k_7k_8k_9[C_2Ph_2]/\{k_{-7}(k_{-8} + k_9)[CO] + k_8k_9[C_2Ph_2]\} \quad (10)$$

if k_{-6} and k_7 are large enough for $[(OC)_4Co\text{-}Co(CO)_3(GePh_2)]$ to be better regarded as a steady-state intermediate. Equation (10) is also consistent with data for reactions under a carbon monoxide atmosphere (provided the term in $[C_2Ph_2]$ in the denominator is sufficiently small), since the intercept of the plot of $[C_2Ph_2]/k_{obs}$ against [CO], 47 ± 92 mol l^{-1} s, could almost as easily be zero as finite, the latter being required by (1)—(4). However, the data for bubbling argon suggest that the mechanism in equations (6)—(9) is less probable. The data require the term in $[C_2Ph_2]$ in the denominator to be much less than the term in [CO] even under conditions where [CO] must be very small; this very small value is also required to be quite constant from run to run since values of $k_{obs}/[C_2Ph_2]$ where $k_{obs} \propto [C_2Ph_2]$ are in good agreement. This requires a rather precisely reproducible balance between the rate of generation of carbon monoxide by the reaction and its rate of removal by bubbling argon.

The mechanism shown in equations (1)—(4) can be contrasted with that for reaction of alkynes with cobalt octacarbonyl. Ungváry and Markó[9] obtained the rate law $-d[Co_2(CO)_8]/dt = k[\text{hept-1-yne}][Co_2(CO)_8]/[CO]$ for reaction in n-heptane and inferred that initial formation of small amounts of the complex $[Co_2(CO)_7(\text{hept-1-yne})]$ in a rapidly established pre-equilibrium is followed by slow loss of another carbon monoxide ligand and formation of $[Co_2(CO)_6(\text{hept-1-yne})]$. However, a more complete study by Ellgen[8] showed that the reaction approaches a limiting rate at high [alkyne] that is related to the rate of dissociative loss of carbon monoxide from cobalt octacarbonyl. Where comparable, the results from Ellgen's studies are in agreement with those from Ungváry and Markó's. At high concentrations of complex and alkyne, Ellgen also obtained kinetic evidence for the formation of a species such as $[Co_2(CO)_7(C_2Ph_2)]$. Ellgen's value of $\Delta S^\ddagger$ for dissociative loss of carbon monoxide from cobalt octacarbonyl was -60 ± 30 J K^{-1} mol^{-1} in comparison with a value of -40 ± 11 J K^{-1} mol^{-1} ascribed[1] to the dissociative reaction of complex (I). It would seem that the positive values of $\Delta S^\ddagger$ expected[17] for dissociative processes must be offset by some sort of compensatory tightening up of the $Co(\mu\text{-}CO)_2Co$ and $Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co$ clusters. The reaction of cobalt octacarbonyl can be understood in terms of attack of alkyne on the complex $Co_2(CO)_7$ formed in the dissociative process, whereas diphenylacetylene does not seem to be capable of attacking $[(OC)_2Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$ to form the same product. The difference probably lies in the readiness of $Co_2(CO_7)$ to exist in the non-bridged form $(OC_3)Co\text{-}Co(CO)_4$ in which the four-co-ordinate d^8 cobalt atom should be quite susceptible to nucleophilic attack by the alkyne. The intermediate $[(OC)_2Co(\mu\text{-}GePh_2)(\mu\text{-}CO)Co(CO)_3]$ cannot, we presume, so readily take up a non-bridged form and attack on the cluster would be sterically less favourable. It seems probable that it is only when a four-co-ordinate d^8 cobalt intermediate is formed by ring opening that attack by diphenylacetylene can occur. The reaction of diphenylacetylene with $[(Bu_3P)(OC)_3Co\text{-}Co(CO)_3(PBu_3)]$ requires[10] either loss of two ligands from the complex, to form $[(OC)_3Co\text{-}Co(CO)_2(PBu_3)]$, or formation of an intermediate that can be formulated as $[(Bu_3P)(OC)_2Co(\mu\text{-}CO)Co(CO)_3(PBu_3)]$, *i.e.* as an analogue of the intermediate $[(OC)_3Co(\mu\text{-}GePh_2)Co(CO)_4]$. The nature of reactive intermediates involved in reactions of alkynes with cobalt carbonyls is therefore very dependent on the detailed nature of the complex. The dependence on the nature of the alkyne has yet to be determined in detail but would be expected also to be varied.

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