A REINVESTIGATION OF THE ISOMERIZATION OF ALKYNE DICOBALT HEXACARBONYL COMPLEXES BY THE PERPENDICULAR-TO-PARALLEL TWIST OF THE ALKYNE: INFLUENCE OF THE INDUCED CARBONYL REORIENTATIONS

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Summary

The isomerization of the $(C_2H_2)Co_2(CO)_6$ complex by the perpendicular-to-parallel twist of the alkyne has been reinvestigated. The large monotonous increase of the energy found earlier by EH calculations turns out not to be due to the twisting process itself but rather to the fact that no allowance was made for relaxation of the carbonyl orientations; upon reorientation of the carbonyls into a trigonal bipyramid geometry about the cobalt centers the increase in energy disappears almost completely. A Mulliken population analysis does not reveal the expected analogy between the reaction with the isomerization of tetrahedrane into cyclobutadiene. Calculations on intermediate structures along a twisting reaction path in which the carbonyls undergo a continuous reorientation induced by the acetylene twist, lead to a state correlation diagram in which a level crossing is observed, allowing the reaction to be classified as symmetry forbidden. The same diagram indicates, however, that there is an upper limit for the activation energy of this isomerization of 117 kJ/mol, a value which can be regarded as within the range of allowed reactions. This result is considered in the light of the available kinetic data on various substitution reactions of $(alkyne)Co_2(CO)_6$ complexes.

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Introduction

The presence of a reactive form of alkyne dicobalt hexacarbonyl complexes [1–3], $acCo_2(CO)_6$, has been suggested, e.g., to explain the results of kinetic studies of the carbon monoxide exchange [4–6] and of the substitution of the carbonyl ligands by phosphines and phosphites [7–9], indicating the existence of an associative pathway. The possibility of such associative pathways opens new perspectives in the elucidation of the mechanism of the alkyne exchange in these complexes [10,11] and of their catalytic properties in the cyclotrimerization of alkynes [12–16].

Until now no detailed proposals have been made for the structure of this reactive form, but its coordinative unsaturation is generally accepted as a strict requirement for permitting associative pathways [17–19]. Such pathways are excluded in the case of the experimentally observed geometry [20–22] of $acCo_2(CO)_6$ by virtue of Tolman's rule [23], since both cobalt centres give an 18 electron count. Moreover, both centres exhibit an octahedral geometry. Even if distorted, as in the present case, this sixfold coordination is not easily expanded to sevenfold coordination [18].

The hypothetical isomeric form of $acCo_2(CO)_6$, able to react by associative pathways, should have an electron count less than eighteen and a coordination number less than six on at least one of the cobalt atoms. The isomerization of the complex from its experimentally observed form into the reactive form could involve either a rupture of the cobalt–cobalt bond or a change of the bonding mode of the alkyne. The former possibility is consistent with the fact that the $acCo_2(CO)_6$ complexes are cluster compounds with a relatively weak metal–metal bond [24]. The latter possibility can be seen as involving migration of the alkyne away from its bridging position in such a way that a vacant site is created on one cobalt atom. This pathway is conceivable since a bridging alkyne is a polydentate ligand [18] capable of lowering the total number of electrons it formally donates to the metals from four to two. Like mononuclear complexes containing a cyclopentadienyl or a nitrosyl ligand, polynuclear acetylene complexes are thus subject to Basolo's qualification of Tolman's rule [26].

In this paper however, we concentrate on an alternative change in the bonding mode of the alkyne, namely the twisting of the alkyne from the perpendicular to the parallel bridging position (Fig. 1). This pathway was excluded recently by Hoffmann et al. [27] on the basis of Extended Hückel (EH) calculations on $(C_2H_2)Co_2(CO)_6$ and analogy with the symmetry forbidden conversion of tetra-
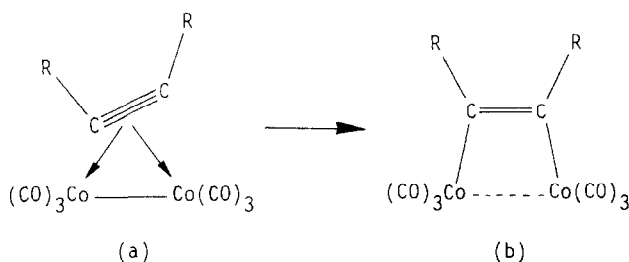

Fig. 1. Schematic representation of the isomerization of the $acCo_2(CO)_6$ complex, from (a) its experimentally observed form with a perpendicular orientation of the bridging alkyne to (b) its hypothetical form with a parallel alkyne orientation.

hedrane into cyclobutadiene. In the present study these arguments are reconsidered, and the alkyne twist reinstated as a plausible isomerization mechanism.

Computational details

Hoffmann's Extended Hückel method [28] was used throughout this work with weighted H_{ij}'s [29]. The parameters were taken from ref. 30 for H, C, and O, and from ref. 27 for Co. The original version of Mulliken's population analysis [31] was used for interpretational purposes. All calculations were performed with the EHT-SPD program [32], which we adapted for use on the CDC CYBER 750–150 computer of the Brussels Free University Computer Center. The following inter-atomic distances and angles were kept fixed throughout: Co–Co, 2.464 Å; C_{ac}–C_{ac}, 1.334 Å; Co–C_{ac}, 2.082 Å; C_{ac}–H, 1.080 Å; Co–CO, 1.805 Å; C–O, 1.133 Å; C_{ac}–C_{ac}–H, 130°; Co–C–O, 180°. Most of these values were taken from the structure of di-t-butylacetylene dicobalt hexacarbonyl [21], and differ only slightly from those cited by Hoffmann et al. [27].

Results and discussion

We first concentrated on the perpendicular form of the $(C_2H_2)Co_2(CO)_6$ complex. In their study, Hoffmann et al. [27] assumed an idealized structure for this form, having a perfect overall C_{2v} symmetry and perfect local C_{3v} symmetry for the $Co(CO)_3$ fragments. When fixed bond lengths and angles within the acetylene and carbonyl ligands are assumed (see Computational Details), these symmetry require-ments permit calculation of the Cartesian coordinates of all atoms from three angles: (a) an umbrella angle, ϕ, between any two carbonyls on the same cobalt atom; (b) the tilt angle [30], θ, between the local C_3 axis of each $Co(CO)_3$ fragment and the Co–Co vector; and (c) the rotation angle, ρ, of each $Co(CO)_3$ fragment about its local C_3 axis. The octahedron-like geometry about the cobalt atoms implies ρ 0°.

The umbrella angle ϕ and tilt angle θ used in ref. 27 were unfortunately not stated, but it can be assumed that the values adapted as in an earlier paper [30] of the same authors were again used, namely ϕ 95° and θ 58.3°. The average experimental values [21] are ϕ 100° and θ 58°. Systematic variation of these angles leads to optimal values of ϕ (103°) and θ (54°). The total energy of this optimized structure ($-156\,499$ kJ/mol) was the lowest among all structures examined in this study, including (a) structures with the acetylene having a perpendicular orientation but with a prism-like geometry (ρ 60°) about one or both cobalt atoms (energies at least 29 and 63 kJ/mol higher, respectively), and (b) all structures with the acetylene having a parallel orientation (vide infra). The lowest-energy structure shows fair agreement with the solid state structures established by X-ray diffraction studies for several alkyne dicobalt hexacarbonyl complexes [20–22], indicating that EH, al-though being very approximate in nature, yields acceptable results for restricted geometry optimizations in this kind of structure.

Turning now to the study of the perpendicular-to-parallel isomerization, we recall that Hoffmann et al. [27] studied a twisting pathway. This pathway was generated by rotating the acetylene moiety of the complex through 90° around the C_2 axis and moving it simultaneously away from the Co–Co vector in order to keep the bond distances of the preserved Co–C_{ac} bonds fixed. The $Co_2(CO)_6$ moiety was kept rigid

during this operation. This led to a progressive increase of the total energy, the energy of the structure with the final, parallel, orientation of the bridging acetylene lying 250 kJ/mol above that of the initial, perpendicular, structure. This large energy increase was considered by Hoffmann et al. to rule out this isomerization pathway, and they attributed it to a decrease in the overlap between several orbitals of the acetylene and $Co_2(CO)_6$ moieties on going from the perpendicular acetylene orientation to the parallel one.

We wondered to what extent the loss of the octahedral geometry about both cobalt atoms might contribute to the energy raise, and so we varied the orientations of the carbonyl ligands, initially still adopting the ideal C_{3v} local symmetry for each $Co(CO)_3$ fragment. It turned out that the carbonyl ligand orientations of the perpendicular structure were far from optimal in the case of the parallel acetylene orientation. A geometry optimization led to a C_{2v} structure with angles ϕ 100°, θ 70° and ρ 60° for both $Co(CO)_3$ fragments, the corresponding energy lowering being 125 kJ/mol. In this optimized structure the geometry about each cobalt atom closely approaches a trigonal bipyramid having an acetylenic carbon in an apical and the other cobalt atom in an equatorial position. The energy of a C_{2v} structure constructed with $Co(CO)_3$ fragments having two angles of 90° and one angle of 120° between the carbonyl ligands, and so with $Co(CO)_3$ fragments well suited to yield trigonal bipyramids with two equatorial and one apical carbonyl ligands, turned out to be optimal when the apical carbonyl was colinear with the $Co-C_{ac}$ bond; the energy of the latter structure with a parallel orientation of the acetylene was only 17 kJ/mol higher than that of the best perpendicular structure. This result shows that the energy increase in the acetylene twist calculated by Hoffmann is almost entirely due to the fact that no allowance was made for relaxation of the carbonyl orientations. This result is in complete agreement with chemical intuition, because since the parallel structure suggests pentacoordinate rather than hexacoordinate cobalt atoms, a trigonal bipyramidal rather than an octahedral surrounding would be expected [25].

At this point, we should emphasize that the energy difference of 17 kJ/mol between the perpendicular and the parallel structures of $(C_2H_2)Co_2(CO)_6$ is still sufficiently high to preclude the observation of the latter structure, as such an energy difference implies that its population would be about 0.1%. This agrees with the interpretation of the existing spectroscopic data [36–38] solely in terms of the perpendicular structure.

Hoffmann et al. [27] also argued against the alkyne twist by showing that this isomerization is an organometallic analogue of the symmetry forbidden conversion of tetrahedrane into cyclobutadiene. This analogy was based on the isolobality [33–35] of CH and $Co(CO)_3$ fragments and on the assumption that the descriptions of the $(C_2H_2)Co_2(CO)_6$ structures with perpendicular and parallel acetylene orientations, such as those in 1,1,1,2,2,2-hexacarbonyldicobaltatetrahedrane and 1,1,1,2,2,2-hexacarbonyl-1,2-dicobaltacyclobutadiene, respectively, are valid. Mulliken population analyses [31] of both structures (Table 1) are however not in agreement with these descriptions. Whereas the Co–Co overlap population suggests a single bond for the structure with the perpendicular acetylene orientation, a striking discrepancy is found for the $C_{ac}-C_{ac}$ bond, which according to the Mulliken overlap population must be a double rather than a single bond. The fact that a description in terms of a double bond is in better agreement with the results of

TABLE 1

MULLIKEN OVERLAP POPULATIONS OF THE $C_{ac}-C_{ac}$, $Co-C_{ac}$, AND Co–Co BONDS IN THE acCo$_2$(CO)$_6$ STRUCTURES WITH PERPENDICULAR (I) AND PARALLEL (II) ACETYLENE ORIENTATION. (The values for the latter are given with the carbonyl orientations used by Hoffmann et al. [27] (II$_1$) and by us (II$_2$). The reference value for a C–C single bond is taken from an EH calculation on ethane; the values for the double and triple C–C bonds in ethene and acetylene are 1.27 and 1.93 respectively [28]. The reference values for Co–C and Co–Co bonds are taken from a Fenske–Hall calculation on Co$_3$(CO)$_9$CH [45].)

Bond	I$_1$	II$_1$	II$_2$	Referene value for a single bond
$C_{ac}-C_{ac}$	1.269	1.303	1.359	0.67
$Co-C_{ac}$	0.253	{ 0.361 { −0.051	{ 0.405 { −0.053	0.50
Co–Co	0.138	0.011	0.048	0.11

X-ray diffraction [20–22], IR [36,38], ^{1}H and ^{13}C NMR [37,38] studies, is a first indication that the description of the perpendicular complex as a dimetallatetra-hedrane might not be adequate. Moreover, the Mulliken overlap populations of the $Co-C_{ac}$ bonds are rather low for single bonds. As a whole, the Mulliken population analysis of the perpendicular complex agrees best with the bonding picture derived from the IR studies [36,38], which has no analogue in organic chemistry. For both structures with a parallel acetylene orientation, the one with the carbonyl orientations proposed by Hoffmann et al. [27] and the one studied by us, the low Mulliken overlap population of the Co–Co bond is hard to reconcile with a double bond, since it is even lower than in the perpendicular structure. Thus, we suggest that there is no bond at all between both cobalt atoms, i.e. that the complex should be regarded as the dimetallated olefin [39] cis-1,2-bis(tricarbonylcobalt)ethene *. Despite the elegance and the widely recognized merits of the concept of isolobality [40], its straightforward application in the present case does not, in our opinion, lead to chemically meaningful results.

As no organic analogue of the perpendicular-to-parallel twist of the acetylene in acCo$_2$(CO)$_6$ complexes seems to exist, the organometallic reaction itself was studied to decide whether the reaction is symmetry allowed or forbidden. Both the perpendicular and the parallel structure have C_{2v} symmetry, but because possible intermediate structures along the twisting pathway have only C_2 symmetry **, only the designation "a" or "b" of the molecular orbitals is relevant [41]. Since with only two classes of orbitals no unambiguous correlation can be drawn between orbitals of both structures based solely upon symmetry considerations, a more detailed study of the reaction path was undertaken. We examined one particular pathway,

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* The absence of a Co–Co bond in the perpendicular structure leads to a fourfold coordination about the cobalt atoms. This revives the question of the geometry of the cobalt atoms. If there is a free electron pair on the cobalt atoms in the position of the formerly assumed Co–Co bond, the proposed trigonal bipyramid is still the right geometry. Otherwise a tetrahedral or square planar geometry seems more appropriate.

** In principle, pathways with only C_1 symmetry must also be considered. As the twisting motion of the acetylene retains the C_2 symmetry, we expect that the induced carbonyl motion does also, and thus that the overall motion does likewise.
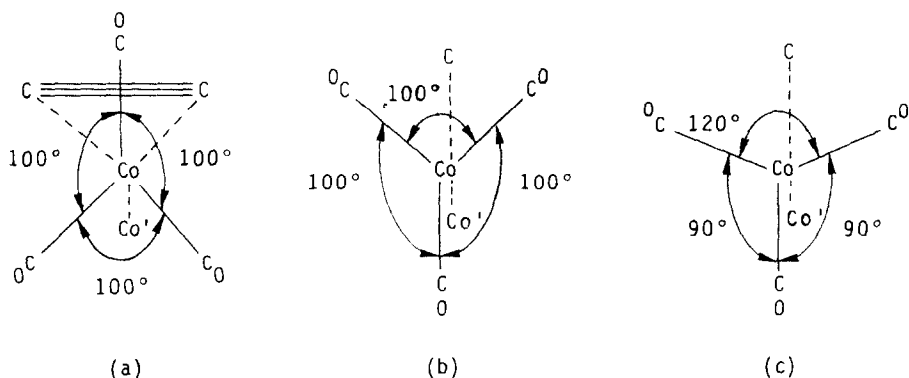
Fig. 2. Projection of a cobalt center along the axis of gravity of the $Co(CO)_3$ fragment in (a) the perpendicular structure, (b) the optimized parallel structure with local C_{3v} symmetry in the $Co(CO)_3$ fragments, and (c) with a trigonal bipyramid-like environment of the Co.

which is identical to that chosen by Hoffmann et al. [27] as far as the motion of the acetylene moiety with respect to the Co–Co vector is concerned, but which includes also a motion of the carbonyl ligands. The motion of the carbonyl ligands induced by the acetylene twist was broken down in our study into three simultaneous simpler motions: (a) the reorientation of the axes of gravity of the $Co(CO)_3$ fragments. Since these axes of gravity almost coincide in the starting (θ 58°) and the final structure (θ 60°), the contribution from this motion is negligible.

(b) the rotation of the $Co(CO)_3$ fragments around their axes of gravity over 60°. When the acetylene approaches its parallel orientation, it pushes away the carbonyl which was originally *trans* to the Co–Co bond, causing this overall rotation of the $Co(CO)_3$ fragments. By itself, this motion would lead to a structure which agrees fairly well with the optimized structure having a parallel acetylene orientation and $Co(CO)_3$ fragments with local C_{3v} symmetry (Fig. 2).

(c) the reorientations within the $Co(CO)_3$ fragments. Because these motions are quite small, the assumption that the carbonyls move within the planes defined by their starting and final orientations was adopted for the sake of simplicity.

The calculations along the reaction path were performed for five intermediate structures, corresponding to rotations of the acetylene about 15, 30, 45, 60, and 75° around the C_2 axis and the corresponding appropriate reorientation of the carbonyls.

The essential part of the resulting correlation diagram is shown in Fig. 3. It reveals that the HOMO of the perpendicular structure substantially increases in energy along the reaction path, and becomes the LUMO of the parallel structure (symmetry type a). In contrast, the LUMO of the perpendicular structure decreases in energy and becomes the HOMO-1 of the parallel structure (symmetry type b). Thus it also crosses the HOMO-1 of the perpendicular structure, which in its turn becomes the HOMO of the parallel structure (symmetry type a). The structure of this orbital correlation diagram suggests that the reaction will be symmetry forbidden. Figure 4 indeed shows that in the derived state diagram a level crossing between two A states occurs.

On one hand, the A ground state of the perpendicular structure correlates with the doubly excited A state of the parallel structure which can be denoted as
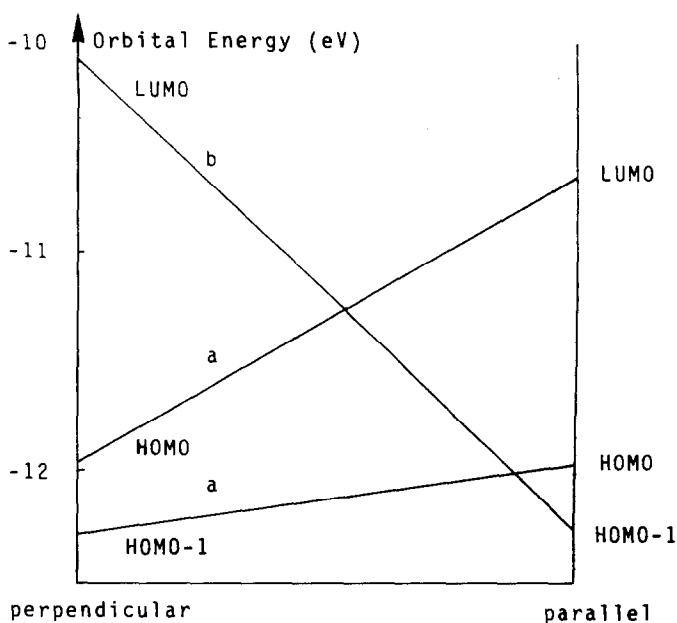
-10 Orbital Energy (eV)

LUMO

b

LUMO

-11

a

HOMO

a

HOMO

-12

HOMO-1

HOMO-1

perpendicular   parallel

Fig. 3. EH calculated orbital correlation diagram for the perpendicular-to-parallel twist of acCo$_2$(CO)$_6$ complexes, showing the correlation between the LUMO, HOMO and HOMO-1 of the initial and final products (no other orbitals are found in the energy region depicted). The dihedral angles between the acetylenic bond and the Co–Co vector is used as the abscissa. Symmetry designations of the orbitals according to the C_2 point group are given.

(HOMO-1 → LUMO)^2, lying 322 kJ/mol above the ground state of the latter. On the other hand, the A ground state of the parallel structure correlates with the A state (HOMO → LUMO)^2 of the perpendicular structure, lying 355 kJ/mol above its ground state. This crossing of two A states allows the studied reaction to be classified as symmetry forbidden.

However, this does not rigorously exclude the possibility that such a reaction can take place. The intended state crossing can, in fact, be avoided via configuration interaction; accordingly the ground state of the perpendicular structure undergoes a transition into that of the parallel structure, following the dashed line in Fig. 4. The extent to which this symmetry forbidden reaction can actually occur is dependent on the height of the energy barrier to be surmounted. Using Lowry's arguments [42], to analyze the data in Fig. 4, in which the correlation between the two corresponding singly excited states of symmetry B is also shown, we estimate a barrier height of 117 kJ/mol (cf. the dashed line in Fig. 4). This value can still be regarded as falling in the range of activation energies for allowed reactions [42–44]. The calculations for the structures along the reaction path indicate an energy increase of at most 192 kJ/mol (with respect to the energy of the perpendicular structure) for the midway structure. In view of the fact that no geometry optimization (e.g. for the carbonyl orientations) was performed for the intermediate structures, and keeping in mind the highly approximate nature of the EH method, the calculated value can be considered as support for our estimate of 117 kJ/mol for the activation energy.

Considering our present results in the light of the available kinetic data on
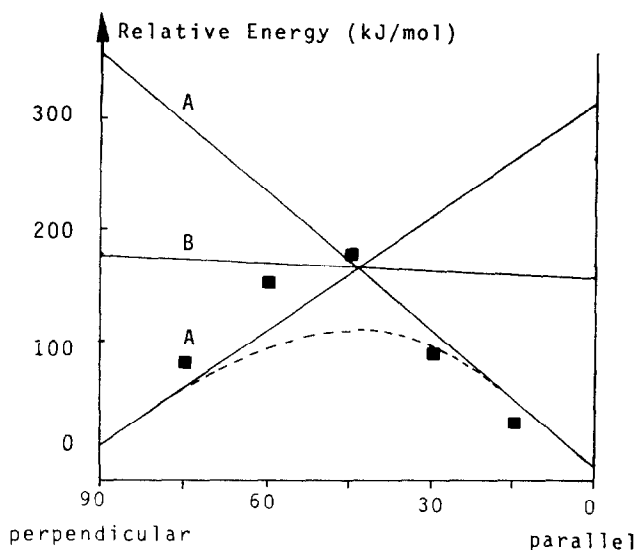
Fig. 4. EH calculated state correlation diagram derived from the data in Fig. 3. Those di-excited states with which the ground states of the initial and final structures correlate together with the corresponding singly excited states B, are shown (full lines). The energies of the actually calculated intermediate structures are also shown (■). The dihedral angle between the acetylenic bond and the Co–Co vector is used as abscissa. Relative energies (in kJ/mol) with respect to the energy of the ground state of the perpendicular structure are given. The symmetry of the states according to the C_2 point group is also indicated.

various substitution reactions of the $acCo_2(CO)_6$ complexes, it seems quite plausible that these are in fact reactions of their parallel form. The observed rate law is, in that case, a combination of the rate law governing the isomerization from the major, unreactive, perpendicular form into the minor reactive parallel form and that for the reaction of the latter form.

The kinetic data on the carbonyl exchange reaction of $acCo_2(CO)_6$ complexes [4–6] lead to the conclusion that this reaction is first order in the complex and zero order in carbon monoxide. The activation energy is about 125 kJ/mol and depends on the electronic effect of substituents of the acetylene: electron withdrawing substituents raise the activation energy for the CO exchange. These results can be interpreted by assuming that the isomerization of the complex is the rate-determining step, in which case the observed rate law is purely that for the isomerization ($k_{obs} = k_1$, Scheme 1).

The interpretation of the kinetic data for the substitution of $acCo_2(CO)_6$ complexes by phosphines or phosphites [7–9] is less straightforward. The substitution of (diphenylacetylene)$Co_2(CO)_6$ by tri-n-butylphosphine was initially interpreted in terms of an equilibrium between the observed form of the complex and an active form, which reacts slowly with the phosphine without disturbing the above equilibrium [7] (Scheme 1). The existence of such a reactive form would be wholly consistent with the isomerization studied in the present paper. The rate law found in this case, $k_{obs} = (k_1 k_2 / k_{-1}) \cdot [L]$, means that the calculated activation energy cannot be compared directly with the experimental data. Later on, the reaction of the same complex with a variety of phosphines and phosphites was reinvestigated [8,9]
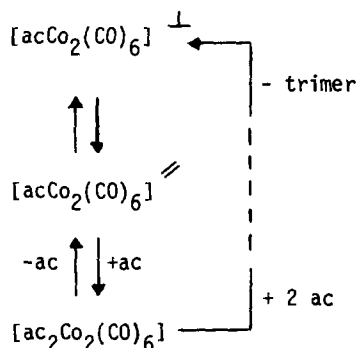
$[acCo_2(CO)_6]^{\perp}$

$k_{-1} \Big\uparrow \Big\downarrow k_1$

$[acCo_2(CO)_6]^{/\!/}$

$k_2 \Big\downarrow + L, -CO$

$acCo_2(CO)_5L$
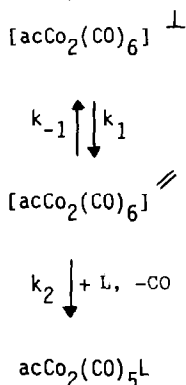
SCHEME 1. Reaction scheme for the carbonyl exchange $(L =^{14} CO)$ and the substitution with phosphines $(L = PR_3)$ and phosphites $(L = P(OR)_3)$. The scheme shows the isomerization of the perpendicular form into the parallel form (with rate constant k_1) and its retro-reaction (k_{-1}) as well as the substitution itself (k_2).

and fitted to a rate law not compatible with our reaction scheme. The approximate data provided are, in our opinion, however, fully consistent with the general rate law implied by Scheme 1.

In the study of the reactions of $acCo_2(CO)_6$ complexes with free alkynes two reactions are observed: (a) exchange between the complexed and the free alkyne, and (b) the cyclotrimerization of the free alkyne catalyzed by the complex (Scheme 2). The former reaction cannot be studied with great accuracy because the latter proceeds at a comparable rate, and interferes by consuming one of the reagents [11,38]. The cyclotrimerization of alkynes by $acCo_2(CO)_6$ has been studied by many workers [12–16], but up to now no kinetic data have been obtained which are sufficiently detailed for comparison with the results presented here. Nevertheless, the similarity of the rates of both reactions is an indication that they have a common rate-determining step.

According to Scheme 2, this may be either the isomerization or the addition of an

$[acCo_2(CO)_6]^{\perp}$ — trimer

$\uparrow\downarrow$

$[acCo_2(CO)_6]^{/\!/}$

$-ac \uparrow \downarrow +ac$

$[ac_2Co_2(CO)_6]$ $+ 2 ac$

SCHEME 2. Reaction scheme for the alkyne exchange and the catalytic cyclotrimerization of alkynes by $acCo_2(CO)_6$ complexes. The former reaction proceeds by both equilibria shown. The latter involves formation of C–C bonds between the two ac ligands in the bottom complex and subsequent reaction which are not shown in detail here [38].

alkyne to the parallel form of the complex. Extrapolation of the kinetic data on the CO exchange reaction [6] leads to a rate constant for the isomerization which is much too large to account for the reaction time of several hours necessary for the completion of a cyclotrimerization [12]. Therefore, we believe that the addition of the free alkyne is the rate-determining step in both the cyclotrimerization and the alkyne exchange.

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