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PHOTOCHEMISTRY OF η^5 -CYCLOPENTADIENYLCOBALT DICARBONYL AND THERMAL DECOMPOSITION OF DERIVED COBALT CLUSTER COMPLEXES. ISOLATION OF BIS(η^5 -CYCLOPENTADIENYLCOBALT) TRICARBONYL, TRIS(η^5 -CYCLOPENTADIENYLCOBALT MONOCARBONYL) AND TETRA(η^5 -CYCLOPENTADIENYLCOBALT) DICARBONYL*

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Summary

The photolysis of η^5 -C₅H₅Co(CO)₂ (XIII) has been found to produce a new, reactive binuclear complex (η^5 -C₅H₅)₂Co₂(CO)₃ as a primary photoproduct; this material has been assigned structure XVII. The material is very labile thermally and decomposes in solution at ambient temperature, releasing a molecule of XIII and forming trinuclear complex (η^5 -C₅H₅CoCO)₃ (XVIII). This molecule is also thermally unstable, and once again decomposes (130°C) with extrusion of XIII, leading in this case to tetranuclear complex (η^5 -C₅H₅)₄Co₄(CO)₂ (XIX). It is proposed that the driving force for cluster complex decomposition arises from the expulsion of a molecule of relatively stable mononuclear metal carbonyl, leaving behind a coordinatively unsaturated intermediate which (in the absence of other reagents) oligomerizes to form a higher, coordinatively saturated cluster. This suggests that in the presence of organic ligands, such decompositions might give rise to active catalysts; in agreement with this idea preliminary studies have shown that complexes XVII and XVIII catalyze acetylene trimerization reactions at temperatures much lower than that required for catalysis by XIII.

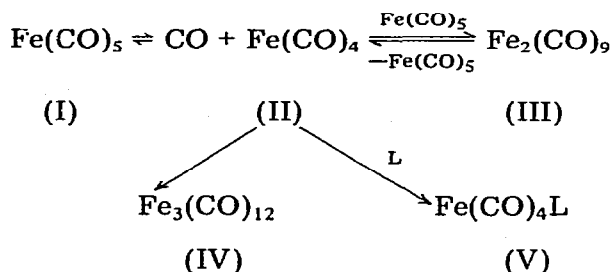
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Introduction

Many metal carbonyl cluster complexes have been prepared in recent years [2], and extensive studies of the intramolecular chemistry (e.g., fluxional carbonyl rearrangements*) and ligand exchange reactions [4] of these complexes have been carried out. Less is known about the details of reactions in which metal-metal bonds in clusters are formed and broken, but the information which is available [2] indicates that such reactions may be quite useful in developing new transition metal systems for use in synthetic and catalytic processes. The behaviour of a classic example such as iron pentacarbonyl (I) illustrates an apparently recurring pattern [5]. Heating or ultraviolet irradiation of I initially causes reversible dissociation of one CO ligand, giving coordinatively unsaturated $\text{Fe}(\text{CO})_4$. This intermediate has three options: it may attack a molecule of

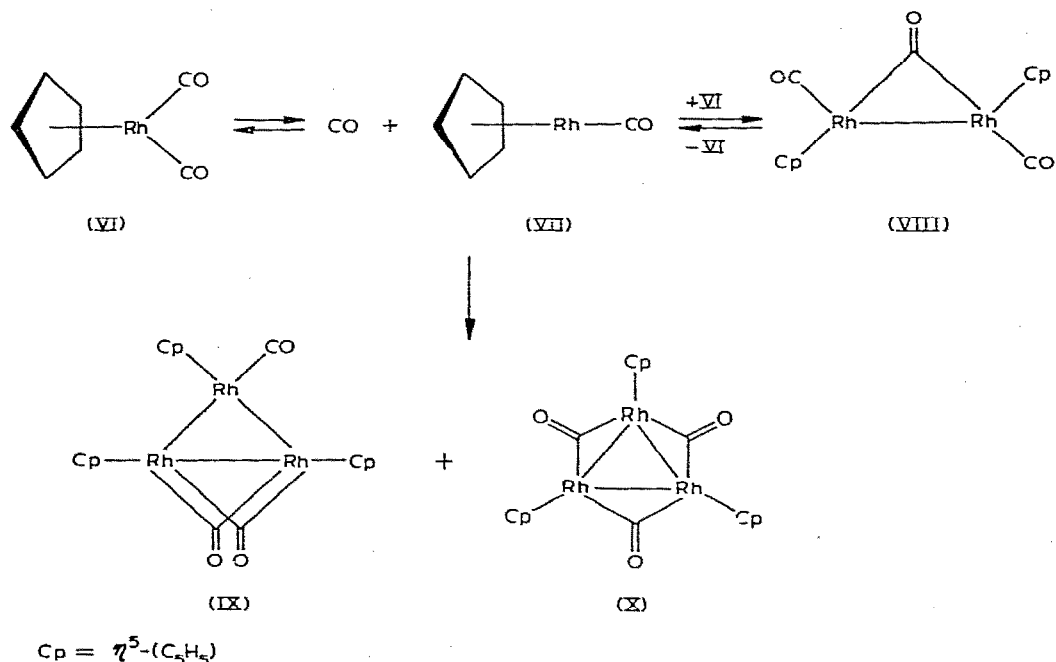


the more stable $\text{Fe}(\text{CO})_5$, leading to $\text{Fe}_2(\text{CO})_9$ (III), coordinate with an external ligand L to give V, or undergo trimerization to $\text{Fe}_3(\text{CO})_{12}$ (IV). Each of these processes converts the 16-electron species II to a more stable, closed shell 18-electron system, and this apparently provides the driving force for such reactions.

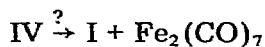
Similar patterns emerge in the chemistry of osmium and ruthenium carbonyls [6], and also in the isoelectronic Rh^I series. For example, irradiation of η^5 -cyclopentadienylrhodium dicarbonyl (VI) leads [7] to the formation of complexes VIII, IX and X. This can be rationalized by again postulating initial dissociation to coordinatively unsaturated intermediate VII, which may either attack a molecule of starting dicarbonyl, giving VIII, or undergo trimerization to IX and X.

Transition metal mediated transformations of organic compounds normally involve the transient generation of coordinatively unsaturated intermediates [8], and two aspects of the chemistry outlined above are therefore of interest regarding the development of potential catalytic and synthetic systems. The first utilizes the fact that binuclear complexes are often much less thermally stable than the parent mononuclear carbonyls [2], and generally decompose by reversal of the II + I type reaction. Thus decomposition of $\text{Fe}_2(\text{CO})_9$ provides a mild method of generating the unsaturated intermediate $\text{Fe}(\text{CO})_4$, and a number of relatively unstable organometallic compounds have been prepared via reactions of organic ligands with $\text{Fe}(\text{CO})_4$ using this technique [9]. The second is that trimeric complexes such as IV or X are also often unstable with respect to extrusion of the mononuclear carbonyl. Using IV as an example, this expulsion of

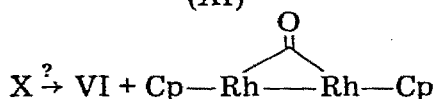
* For a discussion of the mechanism of such rearrangements and a number of references, see ref. 3.



a molecule of $\text{Fe}(\text{CO})_5$ would leave behind complex XI, which contains two adjacent, coordinatively unsaturated 16-electron iron atoms, raising the possibility that such an intermediate might be a potential cooperative or synergistic catalyst for carrying out reactions requiring the proximity of two reactive metal atoms. In the rhodium example outlined below, the analogous reaction would



(XI)

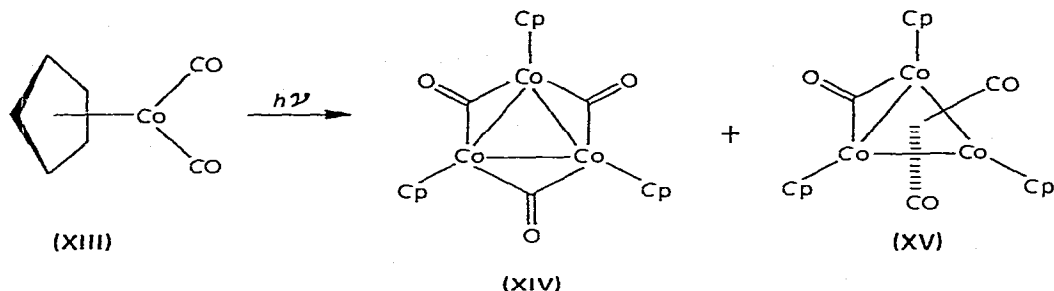


(XII)

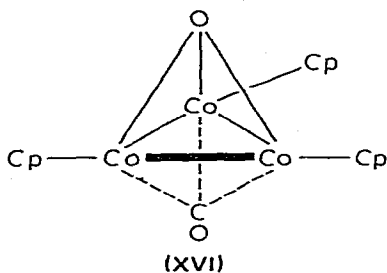
be the generation of VI and XII from X.

Crucial to the development of such processes is the availability of complexes which have been referred to as "lightly stabilized" [10], i.e., stable enough to prepare and handle, but reactive enough to undergo easy decomposition at temperatures near ambient. For this reason, it appeared to us that XIII, the cobalt analog of complex VI, might be an interesting system to investigate, since the strengths of metal-metal bonds between transition metals decrease upon ascending a column of the periodic table [2]. Complex XIII itself has been shown to be a good catalyst for various acetylene trimerization reactions [11]. Our interest in the ultraviolet irradiation of XIII was further stimulated by some apparently conflicting observations which had been reported regarding this reaction. Irradiation of η^5 -cyclopentadienylcobalt dicarbonyl (XIII) was report-

ed by one group [12] to lead to trimers XIV and XV, but irradiation under somewhat different conditions provided a low yield of oxide XVI instead [13].



Finally, when this work was initiated the dinuclear cobalt complex corresponding to VIII had not yet been found. We therefore began a study of the photochemistry of complex XIII. This paper reports the results of that study, along with a few preliminary investigations of acetylene oligomerizations catalyzed by cluster complexes isolated in these reactions.



Results

A 15% solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (XIII) in benzene- d_6 was degassed and sealed in an NMR tube and irradiated at $0\text{-}5^\circ\text{C}$ for 2 h by using a 450 watt Hanovia lamp at $0\text{-}5^\circ\text{C}$. After this time, monitoring by NMR (Fig. 1a) showed a decrease in the intensity of the single line (τ 5.53) exhibited by starting complex XIII (referred to as "peak 1" in Fig. 1 and the following discussion) and the appearance of a new sharp singlet at τ 5.38 (peak 2). Continued irradiation of the sample did not carry the peak 2/peak 1 ratio beyond about 60%. When the irradiated sample was left in the NMR probe (no UV irradiation; temperature ca. 38°C), the new signal began to decrease in intensity with a corresponding regeneration of the signal due to XIII (peak 1). After about 15 min, peak 2 had decreased to about half its original intensity and a second new line (τ 5.36; peak 3) had appeared. Peak 2 continued to decline and 3 stayed about constant until both were of equal height (30 min). Subsequently both 2 and 3 disappeared at about the same rate with a corresponding regeneration of peak 1. The reaction rate slowed considerably after 1 to 2 h; after this time, shaking the sample at 50°C caused essentially complete disappearance of all new peaks and regeneration of peak 1.

In order to rule out the possibility that some or all of these new lines in-

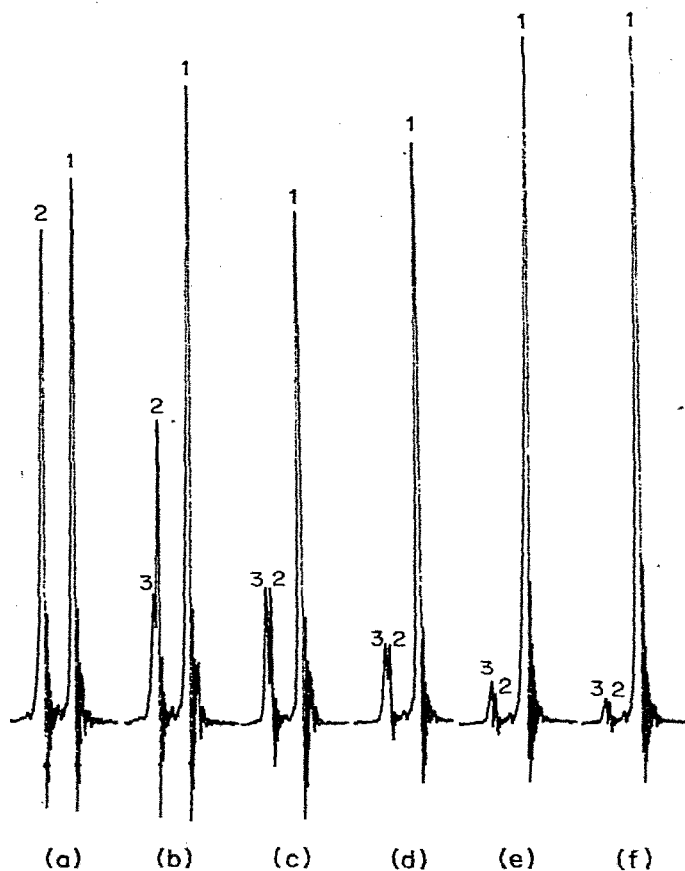


Fig. 1. Changes in the NMR spectrum observed following irradiation of a 15% solution of $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ (XIII) in benzene- d_6 for 2 h (sealed tube). Spectrum a was run at 38°C , 2 min after cessation of irradiation; b 12 min; c 24 min; d 29 min; e 9.5 h at 50°C , f 22 h at 50°C . Spectra a and b were run at a spectrum amplitude of 6.3; spectra c-f were run at spectrum amplitude 5.0.

involved formation of weakly bonded cobalt-benzene π complexes, the irradiation was then carried out in cyclohexane. In this solvent the line for starting complex XIII (peak 1, Fig. 2) appeared at τ 5.08. Upon irradiation a new line again appeared, but this time at a position upfield from XIII (peak 2, τ 5.18); a 50/50 photostationary mixture is ultimately reached. The subsequent dark reaction at 35°C (Fig. 2) again regenerated XIII and produced another new signal (peak 3, τ 5.25), but in this case a third new signal was also observed (peak 4, τ 5.43). As the intensity of peak 2 decayed, 3 reached a maximum concentration at about 50 min. After 20 h XIII had been regenerated, peak 4 had disappeared and only traces of 2 and 3 were left. Once again shaking the sample at 50°C (5 h) produced a clear solution of XIII. This reaction cycle could be repeated several times on the same sample with identical results.

The above NMR study showed that irradiation of XIII led to formation of several new products, all of which (as expected) were characterized by some degree of thermal instability. In order to obtain additional information about

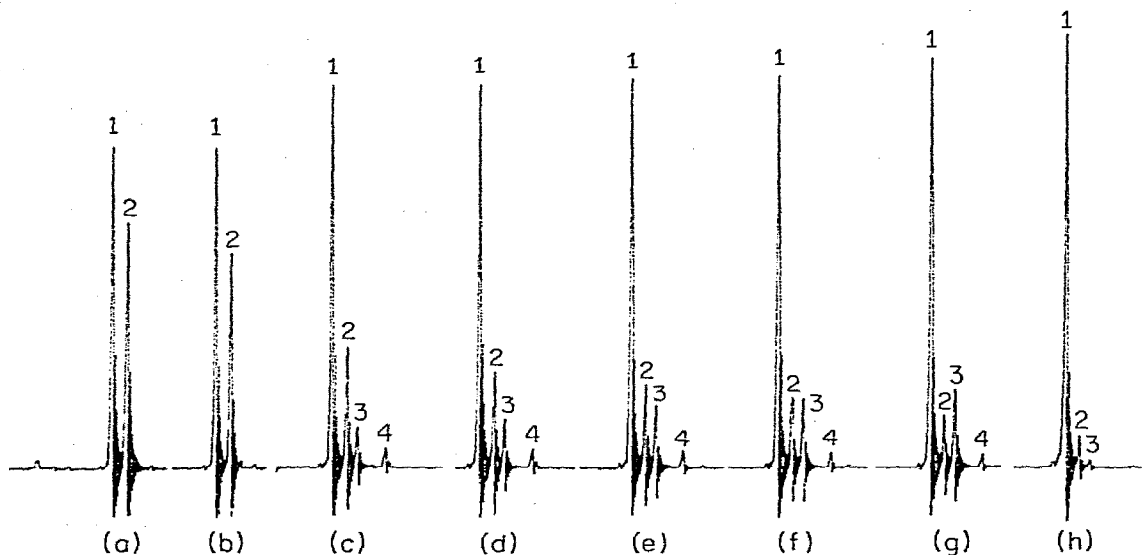


Fig. 2. Changes in the NMR spectrum observed at 38°C following irradiation of 0.5 M $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ (XIII) in cyclohexane for 1 h (sealed tube). Spectrum a was run immediately after cessation of irradiation; b was run after 5 min; c 20 min; d 25 min; e 30 min; f 35 min; g 50 min; h 21 h.

the structures of these materials, the irradiation was repeated in a gas-tight IR cell with sapphire windows. The cell was charged with a degassed 1% solution of XIII in heptane under a nitrogen atmosphere. Complex XIII exhibits two absorptions in the carbonyl region of the infrared due to the symmetric and asymmetric CO stretching modes (ν 2030 and 1970 cm^{-1}); upon irradiation the band at 2030 cm^{-1} decreased in intensity and a new band appeared at 1814 cm^{-1} , indicating the formation of a species containing a doubly bridging carbonyl group. On warming, this band disappeared and the original spectrum was restored; no additional transient bands were observed. This indicated that either all the new materials had only terminal or doubly bridging carbonyls or (more likely) the lower concentrations required for the IR experiment reduced the amounts of minor products formed in the reaction.

We therefore next carried out a preparative run using a somewhat higher initial concentration of XIII. The new carbonyl band at 1814 cm^{-1} suggested that the major photoproduct might be $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ (the cobalt analog of complex VIII). Since this requires loss of one molecule of CO, we therefore also carried out the preparative run under conditions where expelled CO could be pumped away from the reaction mixture. The solution of XIII (7% in methylcyclohexane in a Schlenk-type vacuum apparatus equipped with a sintered filter and bypass) was irradiated under vacuum at 0°C. After several hours the developed CO was pumped off; 0.2 molar equivalents had been liberated. Repetition of this cycle, evaporation of some of the solvent and cooling produced a precipitate of violet crystals (see Experimental). This material was volatile enough for a mass spectrum, which indicated a molecular weight of 332; in the IR it had

bands at 1965 and 1814 cm^{-1} (nujol mull) and 1940 and 1790 cm^{-1} (KBr pellet). In combination with elemental analysis, these data are consistent with an empirical formula of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ (cf. Scheme 1).

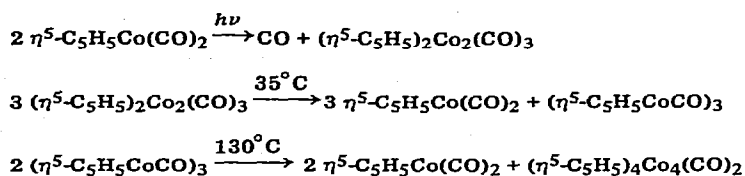
Although $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ was stable in the solid state when stored under inert gas, when dissolved in cyclohexane it immediately began to decompose. Spectroscopic observation of this reaction provided data reminiscent of the results obtained during the dark reaction following irradiation of sealed tubes containing XIII in cyclohexane, despite the fact that in this experiment there was no free CO in the solution when it was initiated. Observation by NMR initially showed the "peak 2" resonance at τ 5.18; this decayed with a corresponding rise in absorptions due to XIII (peak 1) as well as peaks 3 and 4. These latter signals reached maximum intensity after 10 min; they then diminished somewhat and remained constant until the τ 5.18 peak had disappeared. At the same time, black-green crystals precipitated in the NMR tube. After heating several hours the only two signals remaining were due to XIII and peak 3 in a ratio of about 10 to 1. In the IR spectrum of a KBr pellet of this material, changes were noticeable after 10 min at beam temperature, new peaks appearing at 1675, 1835 and 2010 cm^{-1} . Similarly in nujol the band at 1814 cm^{-1} began to disappear as bands at 1760 and 2028 cm^{-1} grew in. Interestingly, a transient peak was observed at 1790 cm^{-1} ; it reached a maximum after 110 min and then disappeared. It is apparently associated with the compound that exhibits the transient peak 4 in the NMR spectral observations.

The green-black crystals formed in the decomposition of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$ were collected and characterized spectroscopically. This complex appears to be similar, but not identical, to the trinuclear complex $(\eta^5\text{-C}_5\text{H}_5\text{CoCO})_3$ (XIV) isolated by King and his co-workers; it can be prepared in better yield by a somewhat modified preparative procedure (outlined in the experimental section). As observed by King, the mass spectrum of this material gave a molecular ion at too large a value (m/e 552, which is consistent with a tetranuclear species; vide infra) under normal heated inlet operating conditions. However, at low inlet temperatures the highest m/e observed is at 456, indicating that the complex undergoes a thermal reaction in the spectrometer inlet system, and its empirical formula is $(\text{CpCoCO})_3$. It exhibits one line in the NMR (τ 5.38) and shows IR absorptions at 1835, 1775, and 1675 cm^{-1} with weaker absorptions at 1805, 1796, and 1755 cm^{-1} ; we observed no absorptions in the terminal carbonyl region for this complex.

As is indicated by the mass spectral study described above, pyrolysis of $(\eta^5\text{-C}_5\text{H}_5\text{CoCO})_3$, like that of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CO})_3$, occurs with extrusion of one molecule of XIII. This reaction is most conveniently carried out by heating the trinuclear complex to 130°C under vacuum in a sublimation apparatus. Under these conditions carbon monoxide is again evolved (0.8 molar equivalents), along with XIII and traces of other complexes. The bulk of the material is left behind in the flask as a black, flaky product which shows a parent molecular ion at m/e 552 in the mass spectrum, indicating that its empirical formula is $(\eta^5\text{-C}_5\text{H}_5)_4\text{Co}_4(\text{CO})_2$. In the NMR it exhibits two signals [τ 5.24 (s, 10H) and 5.35 (s, 10H)]; IR (nujol) 1680, 1665 cm^{-1} .

The transformations outlined in the above discussion are summarized in Scheme 1.

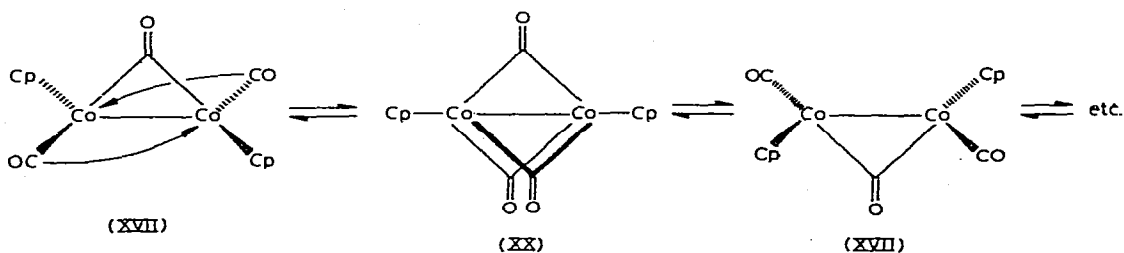
SCHEME 1



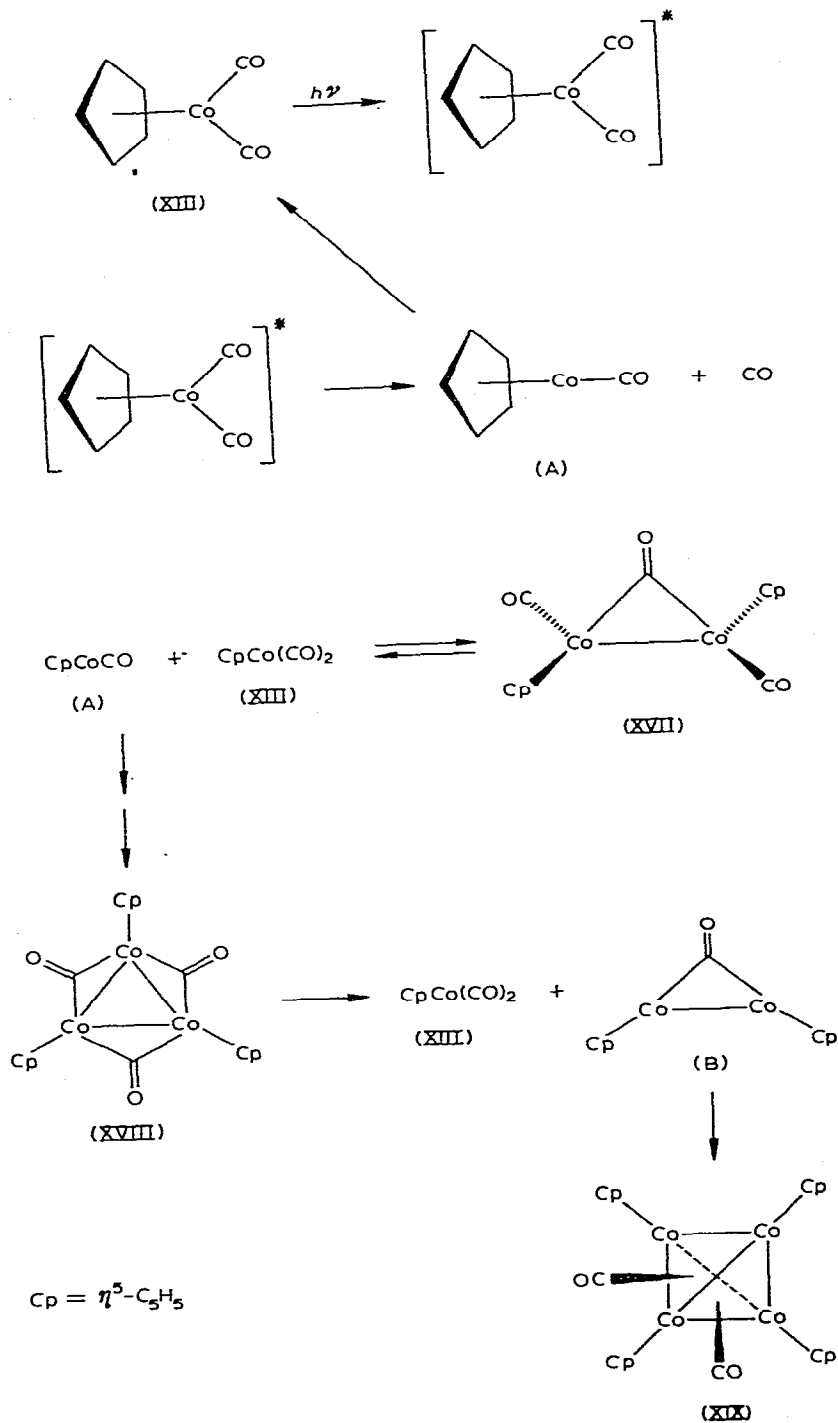
Discussion

The postulate that coordinatively unsaturated mononuclear cobalt complexes and doubly unsaturated binuclear complexes are intermediates in these reactions accounts very nicely for the experimental results reported here; the most likely overall mechanism is outlined in Scheme 2. In analogy to the thermal chemistry [11] of complex XIII, we assume that the initial step in the photochemical reaction involves dissociation of a molecule of CO, leaving coordinatively unsaturated complex A. In the absence of other reactive molecules, this intermediate has three options: it may recoordinate a molecule of CO, returning to XIII, it may undergo trimerization to the closed-shell cluster complex XVIII or it may attack another molecule of XIII, leading to binuclear complex XVII. Under our photochemical conditions (relatively high concentration, sealed NMR tube), the major product-forming pathway appears to be formation of XVII. This material can be isolated, but in solution it undergoes rapid thermal reversion to A and XIII at room temperature.

Mass spectral and analytical data clearly establish the empirical formula of XVII, and the observation of both terminal and doubly bridging carbonyl absorption in the IR (as well as one signal in the proton NMR) confirm its gross structure as that of binuclear complex XVII (cf., Scheme 2). This material is thus the "missing" binuclear complex whose existence might be predicted on the basis of the formation of an analogous complex in the rhodium series [7]. Although we have written the stereochemistry of XVII as *trans*, it is not clear whether the substance is in fact a single stereoisomer or whether it is a rapidly interconverting mixture of *cis* and *trans* isomers. As with its rhodium analog [7e], the molecule is clearly fluxional; in the ^{13}C NMR spectrum it shows only one carbonyl signal down to -60°C . However, if the judgement of Cotton and co-workers concerning the mechanism of carbonyl interchange in binuclear iron complexes can be applied here [3], it seems likely that the reaction proceeds by simultaneous double bridging, leading to intermediate XX, followed by bridge opening. This mechanism requires "backside" or *trans* interaction of the carbo-

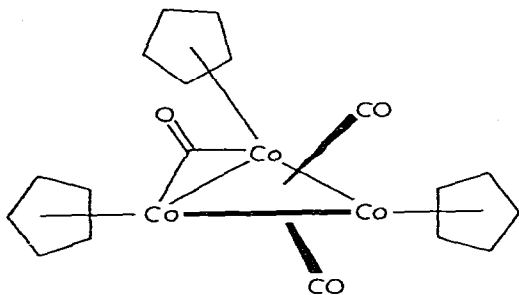


SCHEME 2



nyl groups; hence it cannot provide a mechanism for *cis-trans* isomerization.

Complex XVII is stable in the solid state at room temperature; apparently crystal packing forces are sufficient to repress dissociation. When XVII is dissolved in an inert solvent, however, it rapidly releases a molecule of XIII and now, in the absence of free CO, the remaining coordinatively unsaturated A can only trimerize to XVIII. Once again, analytical and mass spectral data establish its elemental composition. The substance appears to be essentially the complex isolated by King [12], although its IR spectrum does not compare exactly with those of either of his fractions "A" or "B". The most striking difference is that both of King's fractions show some absorption in the terminal carbonyl region (1940 cm^{-1}), whereas our complex XVIII does not. Because this is exactly the absorption position of the terminal carbonyl in XVII, it is most likely that King's samples were contaminated with small amounts of XVII. The source of the other spectral discrepancies is not clear, but in any case both King's and our complex have absorptions near 1675 cm^{-1} , which seems somewhat low to attribute to doubly bridging carbonyls. However, the rhodium analog X, whose structure (at least in the solid state) has been established by X-ray diffraction [7b, c], shows a band at somewhat low frequency (1715 cm^{-1}). If one takes into account the fact that carbonyl absorptions appear at higher frequency in the rhodium (compared to cobalt) binuclear complex [7a] despite similar structures and electronic configurations, the low-frequency 1675 cm^{-1} band in the cobalt trimer may not be inconsistent with the presence of only doubly bridging carbonyls. However, another possibility is that two of the carbonyl groups are not in fact precisely doubly bridging, but have moved off the edges of the cobalt triangle and onto the faces, making them more similar to triply bridging carbonyls. This is basically one of the structures (XV) suggested [12] by King. We assume that in such a species the two "triply bridging" CO's would "lean" toward the unique cobalt atom (as in XXIII), since each of these carbonyls is donating approximately one electron to this cobalt, the other electron being shared by the two "remote" cobalt atoms. Resolution of this structural question must await an X-ray diffraction study.



(XXIII)

The driving force for decomposition of XVII appears to be the energetic favorability associated with reforming a molecule of mononuclear complex XIII. This pattern is apparently followed in the thermal decomposition of trinuclear

complex XVIII. Although the material is inherently more stable than XVII, at its decomposition point it, too, apparently releases a molecule of XIII. Left behind in this case, however, is doubly unsaturated binuclear complex B, which must dimerize to a tetranuclear complex in order to complete the cobalt valence shells. The triply bridging nature of the CO ligands in this complex is rather clearly established by infrared and by the observation of two distinct cyclopentadienyl lines in the proton NMR.

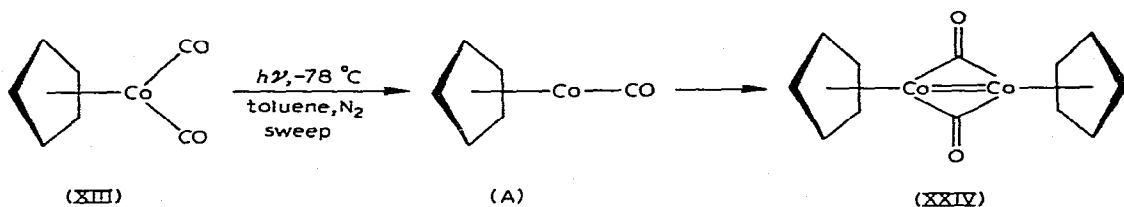
The rapid decomposition of complex XVII, and the apparent fact that both XVII and XVIII give rise on decomposition to coordinatively unsaturated species, suggested that these complexes should be effective catalysts in acetylene trimerization*. We have accordingly carried out a number of preliminary experiments aimed at investigating their potential catalytic utility, employing acetylenes such as 1,5-hexadiyne, 1,6-heptadiyne, phenylacetylene and diphenylacetylene. These studies have shown that complex XVII does in fact catalyze trimerization at much lower temperatures than that required for $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$. Since this reaction proceeds at about the same temperature as that required for dissociation of XVII, we feel certain that dissociation is the primary step in the acetylene trimerization reaction and that $\eta^5\text{-C}_5\text{H}_5\text{CoCO}$ is the active unsaturated catalyst. Details of these studies are given in the Experimental section.

Trinuclear complex XVIII is in many ways an even more interesting potential catalyst, since its thermal conversion to tetranuclear XIX implicates an unsaturated intermediate having two adjacent unsaturated metal atoms. We have found that it, too, effectively catalyzes the trimerization of acetylenes. However, it is not clear that formation of B (cf., Scheme 2) is the first step in this reaction, because the trimerization begins to occur at 65°C in the presence of this material, whereas in the absence of acetylenes decomposition does not proceed in solution at a reasonable rate until the temperature reaches 100°C. It therefore appears that this reaction is somewhat complicated, and may involve initial exchange of acetylene molecules for CO ligands prior to dissociation of the cluster. In accord with this idea, even the thermally very stable tetranuclear complex XIX functions as an acetylene trimerization catalyst with 1,5-hexadiyne, although the temperature required is somewhat higher than that needed for catalysis using XVII and XVIII.

Finally, it should be mentioned that Lee and Brintzinger have recently carried out some very elegant studies [16] on the photochemistry and acetylene trimerization chemistry of XIII, parts of which are complementary to the results reported here. Instead of irradiating in a closed system at room temperature, as we did, Lee and Brintzinger carried out the photolysis of XIII at -78°C in toluene with concurrent sweeping with nitrogen and direct observation by infrared spectroscopy. Under these conditions, dissociated CO is immediately removed from solution and the rate of attack of unsaturated intermediate A on XIII is greatly retarded. The starting complex can be completely destroyed, and a new material with an absorption at 1955 cm^{-1} is observed; this is assigned to the coordinatively unsaturated monocarbonyl A. This material cannot be isolated; when the solution is warmed, in the absence of starting complex XIII, a

* For other examples of cluster-catalyzed acetylene trimerization, see ref. 15.

new complex is formed (IR 1785 cm^{-1}) which can be isolated and on the basis of mass spectral data has composition of a *dimer* of A. The rather unusual structure XXIV has been assigned [15] to this material (we have taken the liberty of



writing it here with a cobalt-cobalt double bond in order to preserve 18-electron configurations for the cobalt atoms); trinuclear complex XVIII is also observed*. In petroleum ether, attack of A on XVIII is apparently not eliminated and formation of binuclear complex XVII is observed even at -78°C . It seems likely that the small amount of transient, unidentified material observed in our experiments, exhibiting an NMR signal at τ 5.43 (this was referred to as "peak 4" in the Results section) in cyclohexane and an IR band at 1790 cm^{-1} in nujol, is in fact the dimer XXIV identified by Lee and Brintzinger [16]. These authors have also isolated a number of complexes formed by reaction of these complexes with acetylenes, and have discussed their possible role in acetylene trimerization processes.

In conclusion, the results reported here clarify the somewhat conflicting earlier reports on the photochemistry of $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2$ (XIII). Two new cobalt cluster complexes have been prepared in this series of reactions (one of them surprisingly unstable), and the formation and empirical formula of a third has been confirmed. The fact that each of these complexes is capable of inducing acetylene trimerization reactions encourages the search for new catalytic systems among cluster complexes. However, it also raises the possibility that clusters might be the active catalysts in thermal reactions of organic molecules which have previously been thought to involve only mononuclear intermediates.

Experimental

General

Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Unless stated otherwise, infrared spectra were taken on Perkin-Elmer IR 225 and 257 instruments and are reported in cm^{-1} . NMR spectra were recorded on either A-60-A or T-60 Varian Associates Analytical NMR spectrometers; chemical shifts are reported in τ units (ppm) with tetramethylsilane (TMS) as internal standard. They are reported as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), J (coupling constant), integration (expressed usually as relative numbers of hydrogens, in a few cases arbitrary relative intensity units). Mass spectra were taken on

* The exact mechanism for transformation of A to trinuclear complex XVIII (Scheme 2) has purposely been left vague; it seems likely (as Lee and Brintzinger suggest) that XXIV is an intermediate in this conversion.

AEI MS 9 and MS 12 spectrometers; spectral peaks are reported as m/e value followed by percentage of base peak. Gas chromatograms were run on either Varian Aerograph 90-P3 or Hewlett Packard 5750 instruments. Columns used: for preparative work, a 10' \times 3/8" glass 20% SE-30 on Chromosorb WAW; for analytical work, a 17' \times 1/8" 30% SE-30 on Chromosorb WAW. All column chromatography was carried out on 200g Woelm neutral Alumina II (200 ml fractions); preparative thin layer chromatography (PTLC) was carried out on Merck Silica Gel F-254.

Bis(η^5 -cyclopentadienylcobalt) tricarbonyl (XVII)

η^5 -C₅H₅Co(CO)₂ (XIII; 1.41 g, 7.84 mmol) in degassed methylcyclohexane (25 ml) was irradiated using a Hanovia 450 watt low-pressure mercury lamp in an evacuated flask attached to a Schlenk-type filtration unit fitted with a by-pass and a second flask. The mixture was cooled during the irradiation so that the flask temperature never exceeded 10°C. After 5.5 h the system was attached to a vacuum line and the developed carbon monoxide removed (Toeppler pump; 0.839 mmol). Irradiation was then continued for another 5.5 h (0.47 mmol CO evolved). Repeating this cycle a third time gave a total of 1.52 mmol CO (39%). The mixture was then warmed, some solvent removed (15 ml) and slowly cooled to -15°C to give violet crystals of air and light sensitive bis(cyclopentadienylcobalt) tricarbonyl (XVII). These were filtered off, washed with methylcyclohexane at -80°C, and dried in vacuo. A total of 150 mg [12%, m.p. < 100°C (dec.)] was obtained. (Analysis: found: C, 46.83; H, 3.19; Co, 35.10. C₁₃H₁₀Co₂O₃ calcd.: C, 47.02; H, 3.04; Co, 35.49%.) Mass spectrum: m/e 332 (M^+ , 0.6%), 304 (0.2%), 276 (0.2%), 180 (35%), 152 (31%), 124 (100%). For IR and NMR, see Discussion.

Tris(cyclopentadienylcobalt monocarbonyl) (XVIII)

Compound XIII (1.30 g, 7.5 mmol) was irradiated in degassed methylcyclohexane (25 ml) as described above. Subsequently the mixture was stirred for 16 h at 35°C; this led to precipitation of black-green crystals. This procedure was repeated three times until no more CO evolved on irradiation (presumably due to the formation of a thin, light-absorbing film on the walls of the reaction vessel). The solvent was removed and unreacted XIII (\approx 0.65 g, 50%) vacuum transferred from the flask. The remaining solid contained starting material and XVIII. Purification was achieved by recrystallization from toluene (after filtration of insoluble material) to give black-green crystals of tris(cyclopentadienylcobalt monocarbonyl) (XVIII) (160 mg, 14%; 28% based on recovered starting material). (Analysis found: C, 47.46; H, 3.43; Co, 38.35. C₁₈H₁₅Co₃O₃ calcd.: C, 47.40; H, 3.32, Co, 38.76%.) Mass spectrum (70°C probe temperature): m/e 456 (M^+ , 2%), 370 (10%), 304 (9%), 276 (100%). IR and NMR spectra, see Discussion.

Tetra(η^5 -cyclopentadienylcobalt) dicarbonyl (XIX)

Trinuclear complex XVIII (67.9 mg, 0.149 mmol) was placed in a sublimation apparatus and heated to 130°C for 50 h. Several thin layers of colored sublimate and the evolution of CO (2.7 ml, 0.12 mmol) and XIII (collected in a liquid N₂ trap) could be observed (see Discussion). The remaining material had

turned into black, flaky crystals of tetra(cyclopentadienylcobalt)dicarbonyl (XIX). (Analysis found: C, 47.32; H, 4.00; Co, 42.19. $C_{22}H_{20}Co_4O_2$ calcd.: C, 47.86; H, 3.65; Co, 42.69%.) Mass spectrum: m/e 552 (M^+ , 3%), 524 (0.7%), 522 (0.9%), 494 (5%), 370 (3.6%), 189 (100%). IR and NMR spectrum, see text.

Reaction of $(\eta^5-C_5H_5)_2Co_2(CO)_3$ (XVII) with 1,5-hexadiyne

In a glove box 10 mg (0.03 mmol) of XVII was placed in an NMR tube fitted with a ground glass joint. The tube was evacuated and 1,5-hexadiyne (50 mg, 0.64 mmol) and benzene- d_6 (0.3 ml) were vacuum transferred into it. The tube was sealed under vacuum, warmed to room temperature, and the reaction monitored by NMR. Rapid changes in the spectrum were observed, indicating the appearance of $\eta^5-C_5H_5Co(CO)_2$ (XIII) and a new peak (τ 5.46). This material disappeared upon warming to 50°C, at which point the product of trimerization of 1,5-hexadiyne [bis(2-benzocyclobutenyl)ethane] [11] began to appear, along with some additional absorptions in the cyclobutene region of the NMR spectrum. The catalytic reaction stopped after about 50% conversion of 1,5-hexadiyne to trimer, presumably due to "drainage" of XVII to inactive cobalt cluster complexes. Preparative thin layer chromatography of the reaction mixture gave only XIII and 1,5-hexadiyne trimer (40% yield).

Reaction of $(\eta^5-C_5H_5CoCO)_3$ (XVIII) with 1,5-hexadiyne and 1-octyne

Preliminary experiments monitored by NMR showed that both trimerization of 1,5-hexadiyne and cotrimerization of this diacetylene with 1-octyne [11] occurred at 80°C in benzene. The reaction was run preparatively in refluxing n-octane; 550 mg (5 mmol) of 1-octyne and 390 mg of the diacetylene were heated at reflux 18 h in 10 ml n-octane in the presence of about 10 mg of XVIII. Thin-layer chromatography showed that none of the mononuclear complex XIII had been formed, and allowed isolation of 1,5-hexadiyne trimer [11] (330 mg) as well as the product of cooligomerization [11], 2-n-hexylbenzocyclobutene (120 mg, 13% yield).

Reaction of XVIII with other acetylenes

1,6-heptadiyne (460 mg, 5 mmol) in degassed benzene (25 ml) was added to a degassed, refluxing solution of XVIII (ca. 50 mg) in benzene (25 ml). After 40 h the solvent was evaporated and the residue chromatographed to give 115 mg (25% yield) of 1,3-bis(2-indanyl)propane [11]. An analogous experiment was run with phenylacetylene (13.5 mg, 0.19 mmol) and XVIII (20 mg, 0.044 mmol). After 50 h at 60°C, the tube was opened; PTLC (silica, pentane/ether, 97/3) gave 1,2,4-triphenylbenzene (10 mg, 75%), spectral data identical with reported values [17].

Reaction of $(\eta^5-C_5H_5Co)_4(CO)_2$ (XIX) with 1,5-hexadiyne

The diacetylene (390 mg, 5 mmol) and XIX (20 mg) were heated at reflux in degassed n-octane under argon for 63 h. PTLC gave three bands (total 150 mg, 39%). The first and major band consisted of the known trimer of the diacetylene [11]; the second and third bands were identified as a tetramer and hexamer of the starting diacetylene.

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