of the nπ^* excited state and the mixing of allowed character into the $\pi^* \leftarrow$ n transition from higher energy transitions polarized in the plane of the molecule.[30]

(6) The carbonyl bond length of CH_3CHO increases ~0.11 Å upon excitation into the ^{1}nπ^* state.

Acknowledgment. This work was supported in part by grants from the National Institutes of Health (R.R.B.), the National Science Foundation (R.R.B.), and the National Center for Atmospheric Research (L.M.H.). L.M.H. gratefully acknowledges a UCAR graduate student fellowship (University Corporation for Atmospheric Research). The authors are grateful to J. A. Bennett for his assistance with the measurement of the laser-induced fluorescence spectrum of acetaldehyde.

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Organocobalt Cluster Complexes. 23. Novel Chemistry of (Acylmethylidyne)- and (Aroylmethylidyne)tricobalt Nonacarbonyl Complexes[1,2]

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Abstract: (Acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes undergo reduction with molecular hydrogen in refluxing benzene with no added catalyst at atmospheric pressure to produce the respective (α-hydroxyalkylidyne)tricobalt nonacarbonyls and, in some cases, the completely reduced alkylidynetricobalt nonacarbonyls. These tricobalt–carbon cluster-substituted ketones also undergo complete reduction to the corresponding alkylidynetricobalt nonacarbonyl when treated with trifluoroacetic acid in refluxing benzene. (Acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes also were found to undergo facile thermal decarbonylation to yield the corresponding (alkylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes. These unusual reactions were attributed to the uniqueness of the C=O bond in these ketones, and a discussion of possible mechanisms is included. In addition, it was found that in refluxing benzene (α-hydroxyalkylidyne)tricobalt nonacarbonyl complexes revert to the respective ketone complexes.

(Acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes, I (Figure 1), are readily accessible by several routes: by the reaction of trichloromethyl ketones, $RC(O)CCl_3$, with dicobalt octacarbonyl[3] and by reaction of (acyliummethylidyne)tricobalt nonacarbonyl reagents, $(OC)_9Co_3CCO^+$,[4,5] with reactive aromatic nucleophiles and with weak organometallic alkylating agents. Such cobalt cluster ketones were important intermediates in our development of the chemistry of organocobalt cluster complexes. Their reduction by triethylsilane, followed by acid hydrolysis (eq 1), provided the corresponding alcohols[6] which

$$RC(=O)CCo_3(CO)_9 \xrightarrow{Et_3SiH} \xrightarrow{\text{concd } H_2SO_4} \xrightarrow{H_2O} RCH(OH)CCo_3(CO)_9 \quad (1)$$

were the precursors of the interesting, highly stabilized cluster carbonium ions, $[RCHCCo_3(CO)_9]^+$.[7] This procedure for $RC(O)CCo_3(CO)_9$ reduction was, however, not applicable to highly hindered systems, e.g., $Me_3CC(O)CCo_3(CO)_9$ and $[(OC)_9Co_3C]_2C{=}O$.

Noteworthy and very intriguing was the fact that the reaction of the cluster ketones with triethylsilane occurred under surprisingly mild conditions. 1:1 Triethylsilane/$RC(O)CCo_3(CO)_9$ reactions carried out in tetrahydrofuran at reflux (~65 °C) under an atmosphere of carbon monoxide for about 8 h gave excellent alcohol yields. As noted in our report of this reaction,[6] silicon hydride addition to ketones generally requires high temperatures, UV irradiation, or transition-metal catalysis. This aspect of the chemistry of the $RC(O)CCo_3(CO)_9$ complexes seemed worthy of closer investigation.

Table I. Reduction of (Acylmethylidyne)- and (Aroylmethylidyne)tricobalt Nonacarbonyl Complexes with Hydrogen

R in $RC(O)CCo_3(CO)_9$	reaction time, h	% yield RCH_2-$CCo_3(CO)_9$	% yield $RCH(OH)$-$CCo_3(CO)_9$
H	3	52	0
CH_3	7	8	31
CH_3CH_2	7	4	23
$CH_3CH_2CH_2CH_2$	6	6	26
p-BrC_6H_4	3	0	79
p-ClC_6H_4	3	0	76
p-FC_6H_4	3	0	83
C_6H_5	3	0	78
p-$CH_3C_6H_4$	2	0	83

The chemistry of the Si—H bond of silicon hydrides in many ways closely parallels that of the H—H bond of molecular hydrogen, especially in the case of transition-metal-catalyzed processes. That being the case, it seemed tempting to consider the possibility of the *direct reduction* of our cobalt cluster ketones by molecular hydrogen. Since their C=O bond is so reactive toward the Si—H function of triethylsilane, their reduction by H_2 might proceed under relatively mild conditions.

Our first experiment[2,8] was carried out with (acetylmethylidyne)tricobalt nonacarbonyl. When this cluster ketone

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(1) Part 22: Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem.* **1980**, *188*, 329.

(2) Preliminary communication: Seyferth, D.; Nestle, M. O.; Eschbach, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 6724.

(3) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265.

(4) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730.

(5) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

(6) Seyferth, D.; Williams, G. H.; Hung, P. L. K.; Hallgren, J. E. *J. Organomet. Chem.* **1974**, *71*, 97.

(7) Seyferth, D.; Williams, G. H.; Eschbach, C. S.; Nestle, M. O.; Merola, J. S.; Hallgren, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4867.

(8) Eschbach, C. S. Ph.D. Thesis, Massachusetts Institute of Technology, 1975.

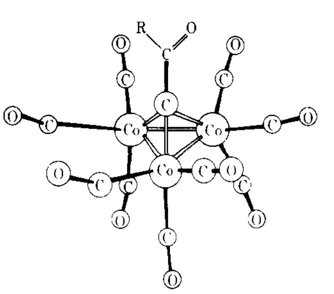


Figure 1. Structure of (acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes.

was heated in benzene solution at reflux while a mixture of molecular hydrogen and carbon monoxide[9] was bubbled through the solution, reduction of the ketone took place and a mixture of the alcohol, $CH_3CH(OH)CCo_3(CO)_9$ (31% yield), and the alkyl, $CH_3CH_2CCo_3(CO)_9$ (75% yield), was produced. This reduction occurred in the absence of an added catalyst and therefore was most surprising. We report here the details of our further investigations of this novel reaction.

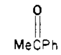
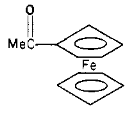
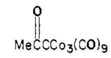
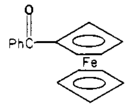
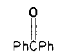
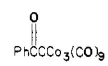
Results and Discussion

Initially, experiments were carried out to determine optimum reaction conditions for the reduction of (acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes with molecular hydrogen. It was found that the highest yields were obtained when the reactions were carried out in refluxing benzene solution while hydrogen and carbon monoxide were bubbled through the solution. The progress of the reactions was monitored by thin-layer chromatography; heating was discontinued when the starting ketone had been completely consumed.

The results of these experiments are given in Table I. The reduction of (aroylmethylidyne)tricobalt nonacarbonyls to the corresponding alcohols occurred rapidly and cleanly, giving the alcohol as the only product in good yield. On the other hand, the reduction of (acylmethylidyne)tricobalt nonacarbonyls with H_2/CO gave the corresponding alkyl, $RCH_2CCo_3(CO)_9$, i.e., the completely reduced product, in low yield, as well as the alcohol. The latter was formed in only moderate yield. The result observed with the formyl compound, $HC(O)CCo_3(CO)_9$, differed still more: only the completely reduced product, $CH_3CCo_3(CO)_9$, was obtained. Thus the reduction to the alcohol is of preparative utility only in the case of the aryl ketones, $ArC(O)CCo_3(CO)_9$.

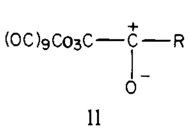
Such hydrogenation reactions which occur so readily in the absence of an external catalyst were very surprising and unusual. A reasonable explanation of these results was one in which the alkylidynetricobalt nonacarbonyl complexes were the source of an active hydrogenation catalyst. Minor decomposition could give $Co_2(CO)_8$ and $HCo(CO)_4$, both known hydrogenation catalysts,[10] and these could then catalyze the reduction of the $RC(O)CCo_3(CO)_9$ complexes to the observed products. If such catalytic species were indeed generated by partial decomposition of these organocobalt cluster carbonyls under the specified reaction conditions, then one might expect them to catalyze the hydrogenation of other ketones which did not contain the $CCo_3(CO)_9$ substituent. Two experiments were carried out to test this idea. In the first, a mixture of 2 mmol of $CH_3C(O)CCo_3(CO)_9$ and 4 mmol of acetylferrocene was treated with H_2/CO in benzene at reflux. Only reduction products of the cobalt cluster complex were obtained; acetylferrocene was recovered in 98% yield. In the second experiment, a mixture of p-$BrC_6H_4C(O)CCo_3(CO)_9$ and acetophenone was hydrogenated with H_2/CO in refluxing benzene. Acetophenone was recovered unchanged, and the cobalt complex was reduced to p-$BrC_6H_4CH(OH)CCo_3(CO)_9$. It would seem that if mono- or dinuclear fragments are generated by partial decomposition of the cobalt clusters, they do not catalyze the hydrogenation of ketones under our reaction conditions or else some hydrogenation of acetylferrocene and acetophenone would have occurred as well. In this connection, it should be noted that hydrogenations catalyzed by $HCo(CO)_4$ and $Co_2(CO)_8$ require much more drastic conditions than those used in this study.[10]

Table II. C=O Stretching Frequencies of Ketones

ketone	$\nu(C{=}O)$, cm^{-1}	ketone	$\nu(C{=}O)$, cm^{-1}
 $MeC(=O)Ph$	1684^a		1672^a
 $MeC(=O)CCo_3(CO)_9$	1640^b		1642^a
 $PhC(=O)Ph$	1658^a		
 $PhC(=O)CCo_3(CO)_9$	1610^b		

[a] From Rosenblum, M. "Chemistry of the Iron Group Metallocenes", Interscience: New York, 1965; p 85. [b] From Seyferth, D. *Adv. Organomet. Chem.* 1976, *14*, 97.

We have no further experimental evidence bearing on the question of mechanism, but some discussion of possible mechanisms is of interest. The ability of the $CCo_3(CO)_9$ substituent to markedly stabilize an adjacent positive charge (as in $[RCHCCo_3(CO)_9]^+$ (ref 7) and $[OCCCo_3(CO)_9]^+$ (ref 4, 5)) was considered a possible explanation for these remarkable reductions. In view of this property of the $CCo_3(CO)_9$ cluster group, canonical structure II may be important in the description of (acylmethylidyne)- and (aroylmethylidyne)tricobalt-nonacarbonyl complexes.



$(OC)_9Co_3C{-}\overset{+}{C}(O^-){-}R$

II

Carbonium ions are known to react with molecular hydrogen ($R^+ \rightarrow RH$), and such hydride abstraction from H_2 could be involved in the present reactions. The facile hydrogenation of the aryl ketones in Table I, in which the positive charge in II could receive additional stabilization from the aryl substituent, would be in line with such an explanation. Also, cobalt cluster complexes containing >C=O functions less capable or incapable of such resonance stabilization (e.g., $EtOC(O)CCo_3(CO)_9$, $CH_3C(O)CH_2CH_2CCo_3(CO)_9$, and p-$CH_3C(O)C_6H_4CCo_3(CO)_9$) were not reduced by the H_2/CO system. One might speculate further that the completely reduced products are produced from the alcohol by loss of a hydroxide ion to form the carbonium ion which could again react with molecular hydrogen (eq 2). The

$$RCH(OH)CCo_3(CO)_9 \rightarrow RC^+HCCo_3(CO)_9,\ OH^- \xrightarrow{H_2} RCH_2CCo_3(CO)_9 + H_2O \quad (2)$$

fact that the alkyl ketones yield $RCH_2CCo_3(CO)_9$ in addition to $RCH(OH)CCo_3(CO)_9$ while the aryl ketones do not may simply be due to the longer reaction times required for their consumption.

Although this simplified view has some attractions, an electronic explanation such as the one above does have some difficulties. The ferrocenylmethylium cations, III, appear to be stabilized to probably a greater extent than the $(OC)_9Co_3C$-substituted carbonium ions.[11] Accordingly, one might expect that ferrocenyl

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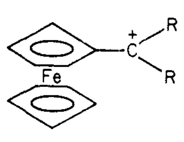
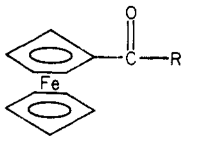
[9] (a) Early during the course of our investigations on $RCCo_3(CO)_9$ complexes we discovered that product yields of reactions carried out above room temperature were much better when carbon monoxide was bubbled through the reaction solution than when the reaction was carried out under a nitrogen atmosphere.[9b] During all of our subsequent studies of the chemistry of $RCCo_3(CO)_9$ complexes we carried out most of the reactions in an atmosphere of carbon monoxide. (b) Seyferth, D.; Hallgren, J. E.; Spohn, R. J.; Williams, G. H.; Nestle, M. O.; Hung, P. L. K. *J. Organomet. Chem.* **1974**, *65*, 99.

[10] (a) Wender, I.; Levine, R.; Orchin, M. *J. Am. Chem. Soc.* **1950**, *72*, 4375. (b) Wender, I.; Greenfield, H.; Orchin, M. *Ibid.* **1951**, *73*, 2656.

[11] Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399.



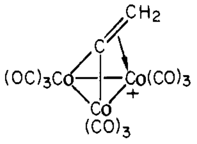
III



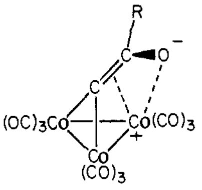
IV

ketones, IV, are polarized to an even greater extent and that they also should react readily with the H_2/CO reagent in benzene at 80 °C. However, both acetyl- and benzoylferrocene are unreactive to H_2/CO under these conditions. Factors other than the electronic effect alluded to may be operative and may enhance the polarization of the C=O bond in the $RC(O)CCo_3(CO)_9$ complexes. Table II shows C=O stretching frequencies for two sets of phenyl, ferrocenyl, and methylidynetricobalt nonacarbonyl ketones. These data are typical, and, in fact, a ν(C=O) as low as 1582 cm^{-1} has been recorded for p-$Me_2NC_6H_4C(O)CCo_3(CO)_9$.[4] While the C=O stretching frequencies of ferrocenyl ketones do not differ very greatly from those of aryl ketones, those of the tricobaltcarbon cluster ketones are much lower.

As the $RCCo_3(CO)_9$ compounds are best viewed as triply bridging carbyne complexes of the $Co_3(CO)_9$ unit, with delocalized bonding,[12,13] so the $(OC)_9Co_3C$-substituted carbonium ions are most advantageously viewed as vinylidenecarbene complexes of the $[Co_3(CO)_9]^+$ moiety, according to MO calculations by Schilling and Hoffmann.[12] The structure of lowest energy found for $[CH_2CCo_3(CO)_9]^+$ was one in which the CH_2 group is tipped toward the Co_3 plane and is circumambulating over it. Formula



V



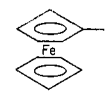
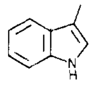
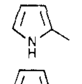
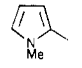
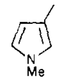
VI

V is a valence bond representation of this structure. If we apply this picture to the cobalt cluster ketones, we could consider VI as an appropriate representation. Although the solid-state structure of $PhC(O)CCo_3(CO)_9$ is unexceptional, with no evidence of any tipping of the PhC(O) substituent from the vertical with respect to the Co_3 plane,[14] it is possible that VI can be achieved in solution. If so, then direct attack by molecular hydrogen on this more open system is a real possibility.

In any case, it seems that this remarkable hydrogenation of $RC(O)CCo_3(CO)_9$ complexes is an intrinsic property of these compounds, i.e., of their unusual C=O bond, rather than the result of the formation of catalytic species of lower nuclearity during the heating period.

Complete reduction of (formylmethylidyne)tricobalt nonacarbonyl to ethylidynetricobalt nonacarbonyl occurred even when the reaction was carried out at temperatures lower than 80 °C. However, aldehydes do, in general, undergo reduction more readily than ketones, and the postulated intermediate carbonium ion, $[CH_2CCo_3(CO)_9]^+$, has been shown to be a stable species.[7] The molecular hydrogen reduction failed in the case of $Me_3CC(O)CCo_3(CO)_9$ and $O{=}C[(CCo_3(CO)_9]_2$,[15] so steric factors can become important.

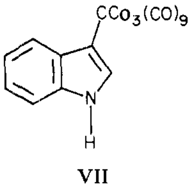
Table III. Thermal Decarbonylation of $RC(O)CCo_3(CO)_9$ Complexes

R in $RC(O)CCo_3(CO)_9$	reaction time, h	% yield of $RCCo_3(CO)_9$
p-$Me_2NC_6H_4$-	0.75	70
p-MeC_6H_4-	6	69
C_6H_5-	5	66
p-FC_6H_4-	30	24
p-ClC_6H_4-	30	19
p-BrC_6H_4-	35	16
 Fe	2	63
 N H	3	71
 N H	10	47
 N Me	5	64
 N Me	6	59
C_2H_5-	18	46
Me_2CH-	4	31
n-C_4H_9-	20	42

An even more unusual chemical property of the $RC(O)CCo_3(CO)_9$ complexes was discovered during the course of our study of the scope of the hydrogenation of this class of compounds. The product which was isolated in the attempted hydrogenation of p-$Me_2NC_6H_4C(O)CCo_3(CO)_9$ with H_2/CO in benzene at 80 °C was neither the alcohol, p-$Me_2NC_6H_4CH(OH)CCo_3(CO)_9$, nor the completely reduced compound, p-$Me_2NC_6H_4CH_2CCo_3(CO)_9$. Rather its proton NMR spectrum indicated it to be p-$Me_2NC_6H_4CCo_3(CO)_9$, i.e., the ketone decarbonylation product. Its identity was confirmed by analysis and by comparison with an authentic sample prepared by the method[9a] shown in eq 3.

$$p\text{-}Me_2NC_6H_4HgCl + HCCo_3(CO)_9 \xrightarrow[CO]{\text{benzene, reflux}} p\text{-}Me_2NC_6H_4CCo_3(CO)_9 \quad (3)$$

In the case of two other cobalt cluster ketones the decarbonylation product was formed in addition to the expected alcohol when they were treated with H_2/CO in benzene solution at 80 °C. In the attempted hydrogenation of (ferrocenoylmethylidyne)tricobalt nonacarbonyl a 31% yield of $C_5H_5FeC_5H_4CCo_3(CO)_9$ was obtained in addition to $C_5H_5FeC_5H_4CH(OH)CCo_3(CO)_9$ (17% yield). Similarly, $Me_2CHCCo_3(CO)_9$ (16%) and $Me_2CHCH(OH)CCo_3(CO)_9$ (3%) were formed in the case of $Me_2CHC(O)CCo_3(CO)_9$. In the case of ((3-indolylcarbonyl)methylidyne)tricobalt nonacarbonyl, treatment with H_2/CO in refluxing benzene also resulted in decarbonylation rather than in reduction to the alcohol. (3-Indolylmethylidyne)tricobalt nonacarbonyl (VII) was obtained in 61% yield.



VII

Such a facile thermal ketone decarbonylation was without precedent in simple, unstrained organic systems and so these observations were of considerable interest. Since carbon monoxide must be eliminated in these reactions, it seemed likely that they would proceed more readily in the absence of external carbon monoxide. This was found to be the case. The yield of p-$Me_2NC_6H_4CCo_3(CO)_9$ obtained when the ketone was heated at 80 °C in benzene solution in a stream of H_2 and CO for 2 h was 41%. In contrast, a 70% yield of the decarbonylation product was obtained when p-$Me_2NC_6H_4C(O)CCo_3(CO)_9$ was heated in benzene solution at 80 °C for only 45 min under a dry nitrogen atmosphere. Further investigation showed that the thermal de-

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[12] Schilling, B. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[13] Miller, D. C.; Brill, T. B. *Inorg. Chem.* **1978**, *17*, 240.

[14] Miller, D. C.; Gearhart, R. G.; Brill, T. B. *J. Organomet. Chem.* **1979**, *169*, 395.

[15] Allegra, G.; Mostardini Peronaci, E.; Ercoli, R. *Chem. Commun.* **1966**, 549.

carbonylation of cobalt cluster ketones is a general reaction. The results of these studies are presented in Table III. The reaction times given are the times required for complete consumption of the starting ketone as indicated by thin-layer chromatographic examination of the reaction mixtures.

Consideration of the results obtained with $ArC(O)CCo_3(CO)_9$ complexes shows that electron-releasing substituents on the aromatic nucleus facilitate the decarbonylation reaction: better product yields are obtained in much shorter reaction times. The same effect was observed with electron-rich heterocyclic substituents on the ketone function. The instability of (acylmethylidyne)tricobalt nonacarbonyls to complete decomposition may be responsible for the lower $RCCo_3(CO)_9$ yields observed in their decarbonylation reactions.

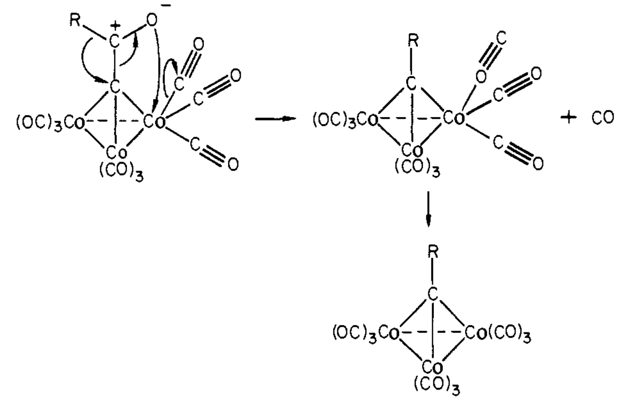
The mechanism of this unusual thermal ketone decarbonylation is of considerable interest. Such decarbonylation is encountered as a free radical process in the Norrish type 1 photochemical fragmentation of ketones in the gas phase and, less commonly, in solution.[16] For instance, in the photochemical decomposition of dibenzyl ketone in solution such decarbonylation and radical coupling to give 1,2-diphenylethane are the predominant processes following α cleavage.[17] Other thermal decarbonylation reactions of ketones are known, but, in general, they proceed via intermediate ketenes and give mixtures of products which are a result of ketene decomposition.[18] The thermal decarbonylation of bridgehead carbonyls in bicyclic systems also is a well-known process. Saturated, bicyclic bridgehead ketones are thermally stable,[19,20] but introduction of unsaturation decreases their thermal stability. Thus substituted bicyclo[2.2.1]hept-2-en-7-ones undergo thermal decarbonylation readily to give high yields of the corresponding 1,3-cyclohexadienes,[19–21] while substituted bicycloheptadienones decarbonylate so readily that attempts to prepare them by Diels–Alder reactions often lead to the isolation of substituted benzenes, i.e., their decarbonylation products.[19,20] However, the thermal decarbonylation of the methylidynetricobalt nonacarbonyl ketones does not seem to fit any of these possibilities. Because of steric factors involving the highly hindered $CCo_3(CO)_9$ group, the C–C bond linking the acyl or aroyl substituents to the tricobalt–carbon cluster may well be rather weak. Therefore, homolytic fission of this bond as a first step in the decarbonylation reaction is not inconceivable. In a previous study, we had shown that the $(OC)_9Co_3C\cdot$ radical can be generated and trapped[22] (eq 4), but all attempts to trap this radical by carrying out the cobalt cluster ketone decarbonylations in allyl ethyl ether or allyl acetate were unsuccessful. These decarbonylations proceeded readily in the dark and were not accelerated by UV irradiation.

$$HCCo_3(CO)_9 \xrightarrow[80\ ^\circ C]{AIBN} \cdot CCo_3(CO)_9 \xrightarrow{CH_2{=}CHCH_2OR} ROCH_2CH_2CH_2CCo_3(CO)_9 \quad (4)$$

$$R = Et \text{ or } Ac$$

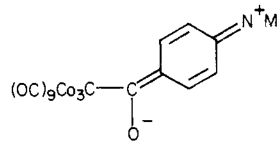
An intriguing question with regard to the mechanism of the decarbonylation of $RC(O)CCo_3(CO)_9$ ketones is as follows: which CO is released in the decarbonylation—the ketone carbonyl group or one of the carbon monoxide ligands on the cobalt atoms? A mechanism in which it is a ligand carbon monoxide which is lost, while the ketone CO is transferred to cobalt is, in fact, an attractive one in that an interaction such as that shown in VI could initiate such a process. Such a mechanism is shown in Scheme I. If CO loss from cobalt was the rate-determining step, one would expect external carbon monoxide to inhibit these decarbonylations. Indeed, bubbling gaseous carbon monoxide through a refluxing benzene solution of $C_2H_5C(O)CCo_3(CO)_9$ prevented the decarbonylation from occurring even to a small extent.

Scheme I



Another experimental observation can find an explanation in terms of the mechanism in Scheme I. It was found that small amounts of acid inhibit the decarbonylation of $RC(O)CCo_3(CO)_9$ complexes. For example, when an attempt was made to carry out the decarbonylation of $Me_2CHC(O)CCo_3(CO)_9$ in acid-washed glassware (rather than the usual glassware cleaned in a base bath), the reaction was found to progress only extremely slowly. After 0.2 mL of alcoholic NaOH had been added to the solution, the thermal decarbonylation occurred at a fast rate. These results were confirmed in experiments with other $RC(O)CCo_3(CO)_9$ compounds. In a control experiment, it was found that the addition of base did not itself accelerate the decarbonylation reaction; apparently, its only purpose was to scavenge traces of acid present. Presumably, then, the acid protonates the ketone C═O function, thus preventing the formation of the key intermediates in Scheme I.

The mechanism shown in Scheme I also serves to explain the results of Table III. The complexes which undergo decarbonylation most readily are those which have an organic function which is capable of electron donation, thus facilitating the interaction of the acyl C═O with the cobalt atom. For example, ((*p*-(dimethylamino)benzoyl)methylidyne)tricobalt nonacarbonyl should have a large contribution from canonical form VIII, which would be favorable for the interaction of type VI. On the other hand, *p*-halophenyl groups withdraw electron density and therefore would be unfavorable for interactions of type VI. Experiments to test the key feature of this proposed mechanism, i.e., the question as to which CO is lost, are contemplated.



VIII

As noted above, traces of acid appear to inhibit the decarbonylation of $RC(O)CCo_3(CO)_9$ complexes. Therefore we reexamined the hydrogenation of those cobalt cluster ketones which had given the decarbonylation product as well as the expected alcohol under the usual hydrogenation conditions, but this time in the presence of added acid. In the case of (ferrocenoylmethylidyne)tricobalt nonacarbonyl as well as of ((2-methylpropanoyl)methylidyne)tricobalt nonacarbonyl, addition of acetic acid to the hydrogenation reaction mixture and use of lower reaction temperatures resulted in formation of the respective alcohol in high yield. For example, reduction of (ferrocenoylmethylidyne)tricobalt nonacarbonyl at 45 °C in the presence of acetic acid (4% by volume) gave a 72% yield of (2-ferrocenyl-2-hydroxyethylidyne)tricobalt nonacarbonyl with no observable decarbonylation. Addition of acetic acid also increased the overall

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(16) Balltrop, J. A.; Coyle, J. D. "Excited States in Organic Chemistry"; Wiley: New York, 1975; pp 180–183.

(17) (a) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074. (b) Robbins, W. K.; Eastman, R. H. *Ibid.* **1970**, *92*, 6076.

(18) Schubert, W. M.; Kinter, R. R. "The Chemistry of the Carbonyl Group", in "The Chemistry of Functional Groups"; Patai, S., Ed., Interscience-Wiley: New York, 1966; pp 735–747.

(19) Allen, C. F. H. *Chem. Rev.* **1945**, *37*, 209.

(20) Allen, C. F. H. *Chem. Rev.* **1962**, *62*, 653.

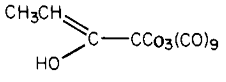
(21) Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of the Carbonyl Group", in "The Chemistry of Functional Groups"; Patai, S., Ed.; Interscience-Wiley: New York, 1966; pp 889–891.

(22) Seyferth, D.; Hallgren, J. E. *J. Organomet. Chem.* **1973**, *49*, C41.

yield of reduced products in the hydrogenation of $C_2H_5C(O)CCo_3(CO)_9$, but the increase occurred almost totally in the yield of the completely reduced product, $CH_3CH_2CH_2CCo_3(CO)_9$. When the hydrogenation of p-$Me_2NC_6H_4C(O)CCo_3(CO)_9$ in benzene was examined in the presence of 4% by volume of trifluoroacetic acid, no reaction occurred until the mixture was heated to reflux, and then, after 8 h, the completely reduced product, p-$Me_2NC_6H_4CH_2CCo_3(CO)_9$, was isolated in 19% yield. Because a quaternary ammonium salt was formed, there seemed to be solubility problems in benzene medium. On changing the solvent to chloroform, under the same reaction conditions, we obtained the completely reduced product in 70% yield. The nature of this reduction is uncertain: first, because the amino function of this ketone forms a salt with trifluoroacetic acid; second, because of further observations on the effect of trifluoroacetic acid on cobalt cluster ketones in the absence of hydrogen. In any case, the addition of a small amount of acetic acid to the reaction mixture in the hydrogenation of $RC(O)CCo_3(CO)_9$ complexes to the alcohols appears to be beneficial in all cases.

Since acid inhibits the decarbonylation of $RC(O)CCo_3(CO)_9$ complexes, the effect of CF_3CO_2H, a strong acid compared to acetic acid, on such cluster ketones was examined. When $C_2H_5C(O)CCo_3(CO)_9$ was heated in benzene solution containing 3% by volume of trifluoroacetic acid under a nitrogen atmosphere, a rapid reaction occurred. The product, $CH_3CH_2CH_2CCo_3(CO)_9$, was unexpected and surprising. A similarly rapid, complete reduction was observed with n-$C_4H_9C(O)CCo_3(CO)_9$. The $RCH_2CCo_3(CO)_9$ yields into these reactions were 50% and 53%, respectively, and reaction times of 1.25–1.5 h sufficed to consume all starting material. (Aroylmethylidyne)tricobalt nonacarbonyls reacted similarly with CF_3CO_2H under these conditions, p-$CH_3C_6H_4C(O)CCo_3(CO)_9$ giving p-$CH_3C_6H_4CH_2CCo_3(CO)_9$ in 12% yield in a reaction time of 6 h, while $C_6H_5CH_2CCo_3(CO)_9$ was obtained in 8% yield in 5 h in such a reaction with the benzoyl cluster.

An attempt to gain some insight into this unexpected, apparently general, reduction process was made by using the reduction of $C_2H_5C(O)CCo_3(CO)_9$ with CF_3CO_2D. The results of this experiment were unexpected: there was complete scrambling of the deuterium between the α- and β-positions of the reduced product, yielding a mixture of $CH_3CHDCHDCCo_3(CO)_9$, $CH_3CH_2CD_2CCo_3(CO)_9$, $CH_3CD_2CH_2CCo_3(CO)_9$, and probably other combinations such as $CH_3CHDCD_2CCo_3(CO)_9$. However, the entire product averaged the incorporation of only two deuterium atoms in each cluster molecule. The incorporation of deuterium into the β-position suggested that the enol form of the ketone, IX, is important in the reduction process.

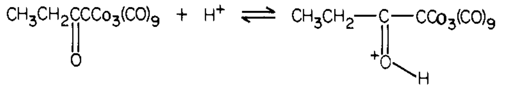


IX

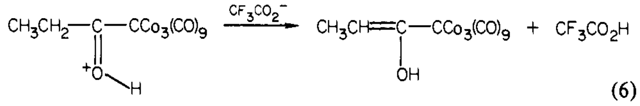
The possibility of such acid-induced enolization was confirmed by experiment. The cluster ketone $C_2H_5C(O)CCo_3(CO)_9$ was treated once again with CF_3CO_2D, but the reduction was allowed to proceed only to 50% completion. The unconverted ketone was isolated and examined spectroscopically. It was found to be almost entirely $CH_3CD_2C(O)CCo_3(CO)_9$.

In order to gain further insight into this unusual reduction process, we investigated various reactions of $CH_3CD_2C(O)CCo_3(CO)_9$. First, the reduction of this ketone with CF_3CO_2D was attempted. However, the reaction proceeded only extremely slowly and therefore the reaction time was so long that a great deal of decomposition took place. The reduced product could not be isolated in sufficient quantity to allow its characterization. A reaction of this ketone with CF_3CO_2H was slower as well, but its rate was sufficiently fast to allow the isolation and characterization of the reduction product. Once again, complete scrambling between the α- and β-positions had taken place to produce a mixture of $CH_3CHDCHDCCo_3(CO)_9$, $CH_3CH_2CD_2CCo_3(CO)_9$, $CH_3CD_2CH_2CCo_3(CO)_9$, and probably various other combinations, again with an average of only two deuterium atoms per cluster molecule. Finally, the reduction of $C_2H_5C(O)CCo_3(CO)_9$ with CF_3CO_2H was carried out in benzene-d_6 as solvent. Only $CH_3CH_2CH_2CCo_3(CO)_9$ was produced, with no deuterium incorporation from solvent.

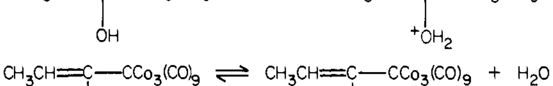
A mechanism for this reduction reaction which involves a (vinylmethylidyne)tricobalt-nonacarbonyl intermediate would account for the observed scrambling of deuterium between the α- and β-positions in the final reduction product. Such a mechanism also would explain why the (aroylmethylidyne)tricobalt nonacarbonyls are relatively unreactive in this CF_3CO_2H-induced reduction: they cannot form stable vinyl derivatives. Equations 5–8 summarize our ideas concerning the initial steps of the reduction process. The vinyl cation IX would be stabilized by the $CCo_3(CO)_9$ substituent. Reaction with a hydride source then would give the vinyl derivative, $CH_3CH{=}CHCCo_3(CO)_9$. The latter, in two further steps, β-protonation and hydride abstraction, could give the completely reduced product. Indeed, we found that the reaction of (isopropenylmethylidyne)tricobalt nonacarbonyl, $CH_2{=}C(CH_3)CCo_3(CO)_9$, with CF_3CO_2D in benzene at reflux resulted in reduction to (2-methylbutylidyne)tricobalt nonacarbonyl, with deuterium incorporation into the α- and β-positions.



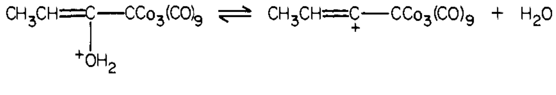
$$\mathrm{CH_3CH_2\underset{\underset{\displaystyle O}{\|}}{C}CCo_3(CO)_9} + \mathrm{H^+} \rightleftharpoons \mathrm{CH_3CH_2{-}\underset{\underset{\displaystyle {}^{+}O{\diagdown}H}{\|}}{C}{-}CCo_3(CO)_9} \qquad (5)$$



$$\mathrm{CH_3CH_2{-}\underset{\underset{\displaystyle {}^{+}O{\diagdown}H}{\|}}{C}{-}CCo_3(CO)_9} \xrightarrow{\mathrm{CF_3CO_2^-}} \mathrm{CH_3CH{=}\underset{\underset{\displaystyle OH}{|}}{C}{-}CCo_3(CO)_9} + \mathrm{CF_3CO_2H} \qquad (6)$$



$$\mathrm{CH_3CH{=}\underset{\underset{\displaystyle OH}{|}}{C}{-}CCo_3(CO)_9} + \mathrm{H^+} \rightleftharpoons \mathrm{CH_3CH{=}\underset{\underset{\displaystyle {}^{+}OH_2}{|}}{C}{-}CCo_3(CO)_9} \qquad (7)$$



$$\mathrm{CH_3CH{=}\underset{\underset{\displaystyle {}^{+}OH_2}{|}}{C}{-}CCo_3(CO)_9} \rightleftharpoons \mathrm{CH_3CH{=}\underset{+}{C}{-}CCo_3(CO)_9} + \mathrm{H_2O} \qquad (8)$$

We can only speculate concerning the source of the hydride ion which is transferred to the two cationic species involved in this suggested mechanism and how the deuterium, introduced into the system in the form of CF_3CO_2D, becomes substituted in part on the carbon atom α to the $CCo_3(CO)_9$ cluster. A reasonable possibility is an intermediate which contains a Co–H (or Co–D) bond, i.e., $HCo(CO)_4$ from partial cluster fragmentation or protonated cluster intermediates, as shown in eq 9–11. It is

$$CH_3CH{=}C^{+}{-}CCo_3(CO)_9 \xrightarrow{[\mathrm{Co{-}H}]} CH_3CH{=}CHCCo_3(CO)_9 \qquad (9)$$

$$CH_3CH{=}CHCCo_3(CO)_9 + H^+ \rightleftharpoons CH_3CH_2C^{+}HCCo_3(CO)_9 \qquad (10)$$

$$CH_3CH_2C^{+}HCCo_3(CO)_9 \xrightarrow{[\mathrm{Co{-}H}]} CH_3CH_2CH_2CCo_3(CO)_9 \qquad (11)$$

noteworthy that reductions of $(OC)_9Co_3C$-substituted ketones with CF_3CO_2H/Et_3SiH produce completely reduced alkyl cluster derivatives in high yield.[6] Thus, when there is a hydride source readily available, as in triethylsilane, these reductions are indeed facile, high-yield processes.

In view of the facile reduction of (acylmethylidyne)tricobalt nonacarbonyls by trifluoroacetic acid all the way to the alkylidynetricobalt nonacarbonyl complexes, it was of interest to see what effect, if any, a much weaker carboxylic acid would have on such $RC(O)CCo_3(CO)_9$ complexes in the absence of molecular hydrogen. It was found that $C_2H_5C(O)CCo_3(CO)_9$ was converted to $C_2H_5CH(OH)CCo_3(CO)_9$ in 58% yield when a benzene solution containing this ketone and an excess of glacial acetic acid was heated at reflux under nitrogen for 2 h. Similarly, $Me_2CHC(O)CCo_3(CO)_9$ was reduced to the alcohol in 41% yield under these conditions. It would seem that the enol produced (as in eq 6) is protonated at carbon and that the resulting carbonium ion, $[CH_3CH_2C(OH)CCo_3(CO)_9]^+$, reacts further by hydride ab-

Table IV. Reactions of $RCH(OH)CCo_3(CO)_9$ in Refluxing Benzene

R in $RCH(OH)CCo_3(CO)_9$	reaction time, h	products (% yield)
Me_2CH	4	$Me_2CHC(O)CCo_3(CO)_9$ (53) $Me_2CHCCo_3(CO)_9$ (10)
CH_3CH_2	12	$CH_3CH_2CCo_3(CO)_9$ (47)
C_6H_5	6	$C_6H_5CCo_3(CO)_9$ (54)
p-$CH_3C_6H_4$	5	p-$CH_3C_6H_4CCo_3(CO)_9$ (49)
p-BrC_6H_4	72	p-$BrC_6H_4CCo_3(CO)_9$ (41)

straction to give the alcohol (as in eq 11).

Because of this unexpected and surprising chemistry, we felt that it was important to show that molecular hydrogen is indeed the reducing agent in the formation of alcohols in the $RC(O)CCo_3(CO)_9 + H_2$ reactions and that no rearrangements were occurring during the reaction. That this was the case was shown by two experiments. Reduction of $PhC(O)CCo_3(CO)_9$ with D_2/CO in refluxing benzene gave $PhCD(OH)CCo_3(CO)_9$ exclusively (the OD exchanges on the silicic acid used in the column chromatographic purification of the product) and the reaction of $CH_3CD_2C(O)CCo_3(CO)_9$ with H_2/CO resulted in formation of $CH_3CD_2CH(OH)CCo_3(CO)_9$ without H/D scrambling.

Finally, one further unexpected and surprising aspect of the chemistry of the $RC(O)CCo_3(CO)_9$ complexes must be mentioned: their reduction to the alcohol by reaction with H_2 is reversible. Thus, for instance, when $Me_2CHCH(OH)CCo_3(CO)_9$ was heated in refluxing benzene solution for 4 h, it reverted to the ketone, $Me_2CHC(O)CCo_3(CO)_9$ (53% yield). In addition, some of the decarbonylation product, $Me_2CHCCo_3(CO)_9$ (10%), was formed. This novel oxidation was found to be a general reaction, although in most cases the ketone formation progressed slowly and decarbonylation of the ketone occurred. The results of the reactions which were carried out are shown in Table IV.

Further work showed that the addition of a small quantity of sodium hydroxide accelerates the alcohol-to-ketone conversion and therefore allows isolation of a moderate yield of the ketone. However, some decarbonylation of the ketone cannot be avoided. For example, a 7-h reflux period served to consume all of the starting materials in a benzene solution containing 1 mmol of $C_2H_5CH(OH)CCo_3(CO)_9$ and 0.2 mL of alcoholic sodium hydroxide. The products isolated were $C_2H_5C(O)CCo_3(CO)_9$ (22%) and $C_2H_5CCo_3(CO)_9$ (16%). In the absence of base, only the decarbonylation product was obtained (cf. Table IV).

In summary, our studies of the $RC(O)CCo_3(CO)_9$ complexes have shown them to be quite unusual, with chemistry which is quite atypical of "ordinary" organic ketones. It is clear that the $Co_3(CO)_9$ moiety to which the RC(O)C unit is bonded has a very significant effect on the chemistry of the carbonyl group of the ketone function. The exact nature of these effects and the mechanisms of the conversions discovered during the course of this work remain unknown and most certainly deserve further study.

Experimental Section

General Comments. Reactions were carried out in an apparatus which was assembled, dried in vacuum and refilled with nitrogen. Solvents were rigorously dried before use and were transferred by syringe or cannula.

The progress of reactions usually was indicated by color changes and was routinely monitored by thin-layer chromatography (TLC) using Eastman silica gel TLC sheet type 6061 and hexane, hexane/dichloromethane (70/30), dichloromethane, or benzene as eluants. The intense colors of the compounds involved made further treatment unnecessary. Mixtures of reaction products in general were separated by column chromatography on silicic acid using hexane, hexane/dichloromethane (70/30), dichloromethane, or benzene as eluants. For separation of samples with widely differing retention times, a filtration chromatography technique was used. A slurry of silicic acid (15–30 cm^3) in the eluting solvent (50–100 mL) was prepared and poured into a filter funnel with a glass frit. Application of aspirator vacuum using a filter flask provided a packed bed of silicic acid for the filtration. The sample then was poured onto the filter pad and washed with hexane until the high R_f material had been completely eluted. Washing the filter bed with dichloromethane then eluted the lower R_f material. Samples recovered from chromatographic separations are reported in the order in which they eluted. Solid samples in general were further purified by sublimation (50–60 °C (0.02–0.07mmHg)) or by recrystallization.

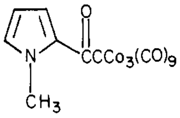
Infrared spectra were recorded by using a Perkin-Elmer Model 337, 237B, 257, or 457A infrared spectrophotometer and proton NMR spectra by using a Varian Associates T-60 spectrometer. Chemical shifts are given in δ units, ppm downfield from internal tetramethylsilane. Tetramethylsilane, dichloromethane, and chloroform were used as internal standards. Deuterium NMR spectra were recorded in the Fourier transform mode utilizing a modified Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system. The field was locked by using the ^{19}F signal of C_6F_6 contained in a capillary inside the sample tube.

Starting Materials. The (acylmethylidyne)- and (aroylmethylidyne)tricobalt nonacarbonyl complexes used in this study either were available in this laboratory or were prepared by methods described in previous papers of this series.[3-5] The following new compounds were prepared.

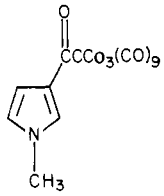
((*p*-Chlorobenzoyl)methylidyne)tricobalt Nonacarbonyl, *p*-$ClC_6H_4C(O)CCo_3(CO)_9$: dark brown crystals; mp 93–95 °C (from hexane); in 16% yield from the reaction of p-$ClC_6H_4C(O)CCl_3$ with $Co_2(CO)_8$ in THF.[3] Anal. Calcd for $C_{17}H_4ClO_{10}Co_3$: C, 35.17; H, 0.69. Found: C, 35.16; H, 0.83.

((*p*-Fluorobenzoyl)methylidyne)tricobalt Nonacarbonyl, *p*-$FC_6H_4C(O)CCo_3(CO)_9$: brown crystals; mp 84–85 °C (from hexane); in 23% yield from the reaction of p-$FC_6H_4C(O)CCl_3$ with $Co_2(CO)_8$ in THF.[3] Anal. Calcd for $C_{17}H_4FO_{10}Co_3$: C, 36.20; H, 0.71. Found: C, 36.33; H, 0.87.

(((*N*-Methylpyrrolyl)carbonyl)methylidyne)tricobalt Nonacarbonyl. A 300-mL three-necked flask equipped with a nitrogen inlet and a magnetic stirring bar was purged with nitrogen and charged with 2.40 g (5.0 mmol) of $ClCCo_3(CO)_9$ and 100 mL of dichloromethane. Aluminum chloride (2.01 g, 15.0 mmol) was added, and the mixture was stirred under nitrogen for 90 min. *N*-Methylpyrrole (1.5 mL) was added; an exotherm was observed and the mixture turned red-brown. The reaction solution was stirred overnight and then was poured into 300 mL of 5% HCl. After the separated aqueous layer had been extracted with 100 mL of CH_2Cl_2, the combined organic phase was dried ($MgSO_4$) and evaporated at reduced pressure. The residue was purified by column chromatography (Mallinckrodt Silicar CC-7, 3:1 hexane/CH_2Cl_2) to yield two products. Each was recrystallized from hexane and each was isolated as dark brown crystals: 1.52 g (58%) of (((2-*N*-methylpyrrolyl)carbonyl)methylidyne)tricobalt nonacarbonyl (X) and 0.67 g (25%) of (((3-*N*-methylpyrrolyl)carbonyl)methylidyne)tricobalt nonacarbonyl (XI). The isomer assignments were made on the basis of NMR spectroscopy and are not absolutely certain. They were made on the basis of the following considerations. (i) The $CCo_3(CO)_9$ substituent would be expected to have less effect on the N–CH_3 when it is in the 3-position than when it is in the 2-position; therefore, the CH_3 resonance in XI should not be as far downfield as that in X. (ii) The isomer XI contains one proton which is sandwiched between the N–CH_3 and the $C(O)CCo_3(CO)_9$ substituent; one would expect this proton peak to be further downfield and well separated from the other two.



X



XI

X: mp 94–95 °C; NMR ($CDCl_3$) δ 4.03 (s, 3 H, CH_3), 6.0–6.3 (m, 1 H), 6.75–7.05 (m, 1 H), 6.95–7.2 (m, 1 H); IR (CCl_4) 2110 (s), 2060 (vs), 2035 (vs), 2020 (sh), 1985 (w) ($Co_3(CO)_9$), 1578 (s), 1570 (sh) (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_6O_{10}NCo_3$: C, 35.00; H, 1.10. Found: C, 35.20; H, 1.18.

XI: melting point, some softening ca. 95 °C followed by decomposition; NMR ($CDCl_3$) δ 3.67 (s, 3 H, CH_3), 6.4–6.65 (m, 2 H), 7.0–7.3 (m, 1 H); IR (CCl_4) 2112 (s), 2065 (vs), 2045 (vs), 2037 (sh), 1982 (sh) ($Co_3(CO)_9$), 1578 (s) (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_6O_{10}NCo_3$: C, 35.00; H, 1.10. Found: C, 34.61; H, 1.31.

Product Identification. Products of the reactions studied were identified by comparison of their melting (or decomposition) points and IR and/or NMR spectra. In most cases authentic samples for comparison were available from previous studies: $RCCo_3(CO)_9$ (R = alkyl and aryl), ref 3 and 9a; $RCH(OH)CCo_3(CO)_9$ and $RCH_2CCo_3(CO)_9$, ref 6 and 7.

Reduction of (Acetylmethylidyne)tricobalt Nonacarbonyl with Molecular Hydrogen. The standard hydrogenation apparatus, which consisted of a 100-mL three-necked, round-bottomed flask equipped with a Friedrichs condenser fitted with a gas inlet/outlet tube, a gas dispersion tube for bubbling hydrogen through the mixture, a glass tube for bubbling carbon monoxide through the mixture, and a magnetic stir bar, was purged with nitrogen and charged with 0.97 g (2.0 mmol) of $CH_3C(O)CCo_3(CO)_9$ and 50 mL of benzene. The solution was flushed with a slow stream of hydrogen and carbon monoxide for 2 h. At this time, TLC showed that no reaction had occurred. The mixture was heated slowly to reflux while the H_2/CO gas streams were continued. After a 7-h reflux period, TLC indicated that all of the starting material had been consumed. The solvent was removed under reduced pressure, and the products were isolated by column chromatography (Silicar CC-7) using benzene as eluant. A great deal of insoluble material remained. The first band to elute yielded 0.08 g (8%) of $CH_3CH_2CCo_3(CO)_9$ (mp 190–192 °C (lit.[6] mp 190–192 °C)) with further identification by comparison of its IR spectrum with that of an authentic sample. The second band to be eluted yielded 0.30 g (31%) of $CH_3CH(OH)CCo_3(CO)_9$ (mp 160–162 °C dec (lit.[6] mp 162 °C dec)) with further identification by IR.

A reaction in which only hydrogen was bubbled through the refluxing $CH_3C(O)CCo_3(CO)_9$ solution gave $CH_3CH_2CCo_3(CO)_9$ in 6% yield and $CH_3CH(OH)CCo_3(CO)_9$ in 17% yield. A reaction carried out in tetrahydrofuran solution (4 h at 35 °C, hydrogen only) gave these products in yields of 6% and 17%, respectively. Acetylferrocene was completely unaffected by hydrogen in benzene solution at reflux during a heating period of 24 h; 0.90 g of the 0.91 g of starting material charged was recovered unchanged. In a competition experiment (2.0 mmol of $CH_3C(O)CCo_3(CO)_9$ and 4.0 mmol of $(CH_3C(O)C_5H_4)Fe(C_5H_5)$ in 50 mL of benzene; 4 h at reflux) the cobalt complex reacted (5% yield of $C_2H_5CCo_3(CO)_9$ and 15% yield of $CH_3CH(OH)CCo_3(CO)_9$), but the acetylferrocene was recovered unchanged in 98% yield.

Reduction of (Formylmethylidyne)tricobalt Nonacarbonyl with Hydrogen. The standard apparatus was purged with nitrogen and charged with 0.94 g (2.0 mmol) of $HC(O)CCo_3(CO)_9$[5] and 50 mL of benzene. The mixture was flushed with H_2/CO for 30 min and then heated to reflux while the gas streams were continued. After 3 h, TLC indicated that the starting material had reacted, producing a purple compound of high R_f. The solvent was removed at reduced pressure, and the residue was purified by column chromatography (Silicar CC-7, benzene eluant) to yield 0.47 g (52%) of $CH_3CCo_3(CO)_9$ (mp 184–185 °C (lit.[23] mp 185 °C)) identified further by its IR and NMR spectra.[9a]

Lowering the reaction temperature to 45 °C (8-h reaction time) led only to a reduced yield (23%) of this product but did not result in the formation of any $HOCH_2CCo_3(CO)_9$.

Reduction of (Propanoyl-α,α-d_2-methylidyne)tricobalt Noncarbonyl with Hydrogen. The apparatus was charged with 0.50 g (1.0 mmol) of $CH_3CD_2C(O)CCo_3(CO)_9$ (for preparation, see below) and 50 mL of benzene. The solution was flushed with hydrogen and carbon monoxide for 1 h and then was heated at reflux for 6 h while the H_2 and CO streams were continued. Workup as above (column chromatography with Silica CC-7, 1:1 hexane/CH_2Cl_2) gave a small quantity of *n*-butylidynetricobalt nonacarbonyl and 0.12 g (24%) of $CH_3CD_2CH(OH)CCo_3(CO)_9$. The IR spectrum of the product was identical with that of $CH_3CH_2CH(OH)CCo_3(CO)_9$. Its NMR spectrum showed that the deuterium had been retained. NMR ($CDCl_3$): δ 1.27 (br s, 3 H, CH_3), 2.32 (d, J = 6 Hz, 1 H, OH), 4.93 (d, J = 6 Hz, 1 H, CH).

Reduction of (Aroylmethylidyne)tricobalt Nonacarbonyl Complexes with Hydrogen. The reduction of ((*p*-chlorobenzoyl)methylidyne)tricobalt nonacarbonyl is described as an example.

The standard hydrogenation apparatus was purged with nitrogen and charged with 0.50 g (0.86 mmol) of $p\text{-}ClC_6H_4C(O)CCo_3(CO)_9$ and 50 mL of benzene. Hydrogen and carbon monoxide were bubbled through the solution for 30 min, and then the mixture was heated to reflux while the H_2 and CO streams were continued. After 3 h at reflux, TLC (3:1 hexane/dichloromethane) indicated that all of the starting material had been consumed and that a purple compound of low R_f had been formed. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (Silicar CC-7, 1:1 hexane/dichloromethane) followed by recrystallization from hexane. A 0.38 g (76%) yield of $p\text{-}ClC_6H_4CH(OH)CCo_3(CO)_9$ (dark brown crystals, mp 111–113 °C) was obtained: NMR ($CDCl_3$) δ 2.68 (d, J = 3 Hz, 1 H, OH), 6.13 (d, J = 3 Hz, 1 H, $C\mathit{H}(OH)$), 7.0–7.6 (m, 4 H); IR (CCl_4) 3590 (m) (OH), 2115 (s), 2065 (sh), 2060 (vs), 2020 (s), 1980 (w) (CO) cm^{-1}. Anal. Calcd for $C_{17}H_6O_{10}ClCo_3$: C, 35.05; H, 1.04. Found: C, 34.99; H, 1.08.

The *p*-fluorophenyl derivative also is a new compound: dark purple crystals; mp 73–74.5 °C; isolated in 83% yield; NMR ($CDCl_3$) δ 2.72 (d, J = 3 Hz, 1 H, OH), 6.20 (d, J = 3 Hz, 1 H, $C\mathit{H}OH$), 6.8–7.7 (m, 4 H); IR (CCl_4) 3585 (m) (OH), 2110 (s), 2067 (vs), 2055 (vs), 2030 (sh), 1977 (w) (CO) cm^{-1}. Anal. Calcd for $p\text{-}FC_6H_4CH(OH)CCo_3(CO)_9$,$C_{17}H_6O_{10}FCo_3$: C, 36.07; H, 1.07. Found: C, 36.22; H, 1.23.

Attempted Reduction of ((*p*-(Dimethylamino)benzoyl)methylidyne)tricobalt Nonacarbonyl with Hydrogen. The standard apparatus was purged with nitrogen and charged with 1.0 g (1.7 mmol) of $p\text{-}Me_2NC_6H_4C(O)CCo_3(CO)_9$ and 50 mL of benzene. Hydrogen and carbon monoxide were bubbled through the mixture for 30 min, and then the solution was brought to reflux while the gas streams were continued. After 2 h, TLC (benzene) indicated that the starting material had been consumed. After the solvent had been removed at reduced pressure, the residue was purified by column chromatography (Silicar CC-7, benzene) and subsequent recrystallization from hexane to give 0.46 g (41%) of $p\text{-}Me_2NC_6H_4CCo_3(CO)_9$: green crystals; mp 125–126 °C (the color of the solid is surprising since solutions of this compound are dark orange); NMR ($CDCl_3$) δ 3.09 (s, 6 H, CH_3), 6.99 (AA′BB′, m); IR (CCl_4) 2100 (m), 2051 (vs), 2038 (s), 2017 (m), 1970 (w) (CO) cm^{-1}. Anal. Calcd for $C_{18}H_{10}NO_9Co_3$: C, 38.53; H, 1.80; N, 2.50. Found: C, 38.65; H, 1.92; N, 2.50. The NMR spectrum is in good agreement with the spectrum reported by Dolby and Robinson for this compound.[24]

This product was in all respects identical with a sample of authentic $p\text{-}Me_2NC_6H_4CCo_3(CO)_9$ prepared as described below by using a procedure for $ArCCo_3(CO)_9$ developed earlier in these laboratories.[9a]

A similar reaction carried out at 40 °C for 8 h instead of 80 °C gave $p\text{-}Me_2NC_6H_4CCo_3(CO)_9$ in 62% yield. At room temperature, during a 5-day period, no reaction occurred when an H_2/CO stream was passed through a benzene solution of $p\text{-}Me_2NC_6H_4C(O)CCo_3(CO)_9$, but decomposition to insolubles was extensive. The recovery of starting material was only 21%.

In another experiment, 0.59 g (1.0 mmol) of $p\text{-}Me_2NC_6H_4C(O)CCo_3(CO)_9$, 50 mL of benzene, and 2 mL of trifluoroacetic acid were charged into the standard apparatus, and the mixture was saturated with H_2 and CO. The reaction mixture then was stirred and heated to reflux while the H_2/CO streams were continued. The progress of the reaction was followed by withdrawing a small aliquot, neutralizing it with dilute sodium bicarbonate, and checking the organic layer by TLC (benzene). After 8 h the reaction mixture was poured into aqueous 3% sodium bicarbonate. The organic layer was dried ($MgSO_4$) and concentrated, and the residue was purified by column chromatography (Silicar CC-7, benzene). The first component (0.11 g, 19%) was $p\text{-}Me_2NC_6H_4CH_2CCo_3(CO)_9$: dark purple crystals; melting range 90–120 °C (lit.[7] melting range 90–105 °C); identified by means of its IR and NMR spectra. Also isolated was 0.33 g (56% recovery) of the starting ketone, apparently because of the limited solubility of the quaternary ammonium acetate.

This reaction was repeated on the 1.0-mmol scale in 50 mL of reagent grade chloroform and 2 mL of trifluoroacetic acid. After 8 h of reflux, the reaction mixture was worked up as above to give 0.40 g (70%) of $p\text{-}Me_2NC_6H_4CH_2CCo_3(CO)_9$.

Preparation of (*p*-(Dimethylamino)benzylidyne)tricobalt Nonacarbonyl. With use of the procedure of Pesci,[25] (*p*-(dimethylamino)phenyl)mercuric acetate was prepared in 94% yield from 30 g of $Hg(OAc)_2$ in 200 mL of 50% ethanol and 50 g of *N*,*N*-dimethylaniline in 96% ethanol. This mercurial then was converted to the chloride by shaking it with aqueous sodium chloride. The water layer was extracted with diethyl ether; the extracts were dried over $MgSO_4$ and evaporated at reduced pressure to give 32.4 g of (*p*-(dimethylamino)phenyl)mercuric chloride, mp 223–225 °C dec (lit.[26] mp 224 °C dec).

A 100-mL three-necked flask equipped with a magnetic stirring assembly, a reflux condenser fitted with a nitrogen inlet, and a glass tube for bubbling carbon monoxide through the reaction solution was purged with nitrogen and charged with 0.88 g (2.0 mmol) of $HCCo_3(CO)_9$, 1.44 g (4.0 mmol) of $p\text{-}Me_2NC_6H_4HgCl$, and 50 mL of benzene. Carbon monoxide was bubbled through the mixture for 30 min, and then it was heated at reflux while the CO stream was continued. After 6 h TLC (hexane) indicated that the starting material (purple spot) had been consumed and that a new product (orange spot) was present. The mixture was cooled and filtered and the filtrate evaporated at reduced pressure. Column chromatography (silicic acid, hexane) followed by recrystallization from hexane gave 0.87 g (78%) of $p\text{-}Me_2NC_6H_4CCo_3(CO)_9$.

Reduction of (Ferrocenoylmethylidyne)tricobalt Nonacarbonyl with Hydrogen. Hydrogen and carbon monoxide were bubbled through a refluxing solution of 2.31 g (3.5 mmol) of (ferrocenoylmethylidyne)tri-

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cobalt noncarbonyl in 50 mL of benzene by using the procedure described above. After 3 h, TLC (benzene) showed that the starting material had been consumed. After workup as in the previous experiments the product was purified by column chromatography (Silicar CC-7, 1:3 dichloromethane/hexane). The two components which were isolated were recrystallized from hexane to give 0.69 g (31%) of (ferrocenylmethylidyne)tricobalt nonacarbonyl, $C_5H_5FeC_5H_4CCo_3(CO)_9$ (red-purple crystals; mp 75.5–77.0 °C (lit.[9a] mp 75–77 °C); NMR spectrum identical with that of an authentic sample), and 0.38 g (17%) of (2-ferrocenyl-2-hydroxyethylidyne)tricobalt nonacarbonyl, $C_5H_5FeC_5H_4CH(OH)CCo_3(CO)_9$, brown crystals which decompose on being heated without melting. NMR ($CDCl_3$): δ 2.97 (br s, 1 H, OH), 4.07–4.51 (m, Cp, 9 H), 5.80 (br s, 1 H, Co_3CCH). Anal. Calcd for $C_{21}H_{11}O_{10}FeCo_3$: C, 38.74; H, 1.93. Found: C, 38.45; H, 1.69.

The alcohol was the exclusive product when the reduction was carried out in the presence of acetic acid. Hydrogen and carbon monoxide were bubbled into a solution of 0.65 g (1.0 mmol) of (ferrocenoylmethylidyne)tricobalt nonacarbonyl and 2 mL of glacial acetic acid in 50 mL of benzene at room temperature for 1 h. Then the mixture was heated gradually until TLC indicated that reduction was occurring—at ca. 40–45 °C. After 8 h of reaction (continued H_2/CO stream) at this temperature, workup as in the previous experiment, 0.45 g (72%) of $C_5H_5FeC_5H_4CH(OH)CCo_3(CO)_9$ (identification by IR and NMR) was obtained.

Reduction of (2-Methylpropanoylmethylidyne)tricobalt Nonacarbonyl with Hydrogen. The reduction of 1.54 g (3.0 mmol) of $Me_2CHC(O)CCo_3(CO)_9$ in 50 mL of benzene with hydrogen and carbon monoxide at 80 °C (5.5 hr.) was carried out as in the experiment above. Column chromatography of the solid residue (Silicar CC-7, benzene) gave 0.23 g (16%) of $Me_2CHCH_2CCo_3(CO)_9$, whose IR and NMR spectra were identical with those of an authentic sample,[6] and 0.046 g (3%) of $Me_2CHCH(OH)CCo_3(CO)_9$ (mp 113–115 °C (lit.[6] mp 114–116 °C)) also identified by its IR and NMR spectra.[6]

A similar reaction carried out with 2.0 mmol of $Me_2CHC(O)CCo_3(CO)_9$ in 50 mL of benzene in the presence of 2 mL of glacial acetic acid gave, after H_2/CO had been bubbled into the solution at 45 °C for 6 h, 0.04 g (4%) of $Me_2CHCH_2CCo_3(CO)_9$ and 0.62 g (60%) of $Me_2CHCH(OH)CCo_3(CO)_9$.

Reduction of (Benzoylmethylidyne)tricobalt Nonacarbonyl with Deuterium. The standard apparatus was charged with 1.10 g (2.0 mmol) of $C_6H_5C(O)CCo_3(CO)_9$ and 50 mL of benzene. Deuterium, D_2, and CO were bubbled through the solution for 30 min, and then the mixture was heated to reflux while the D_2/CO gas streams were continued. The reaction proceeded very slowly (TLC). After 6 h two products were present which on TLC gave a brown spot of high R_f and a purple spot of low R_f (1:3 CH_2Cl_2/hexane). After removal of the solvent, column chromatography (Silicar CC-7, 3:1 hexane/CH_2Cl_2) yielded 0.33 g (32%) of $C_6H_5CCo_3(CO)_9$ and 0.39 g (36%) of $C_6H_5CD(OH)CCo_3(CO)_9$, which had an IR spectrum identical with that of $C_6H_5CH(OH)CCo_3(CO)_9$ and the following NMR spectrum ($CDCl_3$): δ 2.70 (br s, 1 H, OH), 7.1–7.8 (m, 5 H). The NMR spectrum of $C_6H_5CH(OH)CCo_3(CO)_9$, for comparison, shows the following: δ 2.72 (d, 1 H, OH), 6.20 (d, 1 H, Co_3CCH), 7.42 (m, 5 H).

Decarbonylation Reactions. The $RC(O)CCo_3(CO)_9$ complex (1–2 mmol) and about 50 mL of benzene were charged into a 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser fitted with a nitrogen inlet tube. The resulting solution was stirred and heated at reflux until TLC showed that the starting material had been consumed. The solvent then was removed at reduced pressure, and the product was isolated by column or filtration chromatography or by recrystallization. Table III lists the $RC(O)CCo_3(CO)_9$ complexes studied, the required reflux times, and the products and their yields.

The following new compounds were characterized. (3-Indolylmethylidyne)tricobalt nonacarbonyl (VII): mp 154–156 °C dec; NMR (CCl_4) δ 7.0–8.2 (m). The IR spectrum (in CCl_4) showed the N–H stretch at 3479 cm^{-1} and the cluster CO bands at 2100 (m), 2040 (vs), 2020 (m), 1990 (sh), and 1970 cm^{-1} (sh). Anal. Calcd for $C_{18}H_6O_9NCo_3$: C, 38.81; H, 1.09; N, 2.51. Found: C, 38.76; H, 1.32; N, 2.57. (2-Pyrrolylmethylidyne)tricobalt nonacarbonyl: brown crystals; decomposition above 110 °C without melting; NMR ($CDCl_3$) δ 6.0–7.3 (m, maxima at 6.2, 6.4, 6.8, and 7.2 ppm); IR (CCl_4) 3480 (m) (N–H), 2100 (m), 2042 (vs), 2018 (s), 1986 (sh), 1976 (w) (CO) cm^{-1}. Anal. Calcd for $C_{14}H_4O_9NCo_3$: C, 33.17; H, 0.80. Found: C, 32.98; H, 0.99. ((2-*N*-methylpyrrolyl)methylidyne)tricobalt nonacarbonyl (X): brown crystals; mp 149–151 °C dec; NMR ($CDCl_3$) δ 3.70 (s, 3 H, CH_3), 5.95–6.2 (m, 1 H), 6.35–6.55 (m, 1 H), 6.65–6.9 (m, 1 H). Anal. Calcd for $C_{15}H_6O_9NCo_3$: C, 34.58; H, 1.16. Found (for a mixture of the 2- and 3-isomers): C, 34.58; H, 1.16. ((3-*N*-methylpyrrolyl)methylidyne)tricobalt nonacarbonyl (XI): brown crystals; mp 107.5–109 °C; NMR ($CDCl_3$) δ 3.63 (s, 3 H, CH_3); 6.15–6.4 (m, 1 H), 6.4–6.6 (m, 1 H), 6.65–6.85 (m, 1 H).

Some control experiments deserve mention.

The ketone $C_2H_5C(O)CCo_3(CO)_9$ remained unchanged (TLC) when its benzene solution was heated at reflux while carbon monoxide was bubbled through it for 12 h. However, when the CO stream was discontinued, the decarbonylation product, $C_2H_5CCo_3(CO)_9$, was apparent (TLC) after 1 h of reflux. After 16 h of reflux under a nitrogen atmosphere, the ketone had been consumed and the standard workup gave the decarbonylation product in 34% yield.

The decarbonylation of *p*-$Me_2NC_6H_4C(O)CCo_3(CO)_9$ proceeded as readily in the dark as in ordinary laboratory light, giving a 67% yield of *p*-$Me_2NC_6H_4CCo_3(CO)_9$ after a 1-h reflux period in benzene solution. (The flask was wrapped in aluminum foil to exclude light.)

A solution of 1.5 mmol of $PhC(O)CCo_3(CO)_9$ in 50 mL of benzene remained unchanged after 24 h of UV irradiation. The apparatus used consisted of a quartz container surrounded by a quartz condenser. This was fitted with a magnetic stirring unit and a two-hole rubber stopper. One hole was used to introduce a nitrogen inlet tube; the other was kept stoppered and was used for occasional withdrawal of samples for TLC. Cold water was run through the condenser to keep the reaction mixture cool. The recovery of starting ketone was quantitative. A similar observation, i.e., no reaction, was made in the attempted UV-induced decarbonylation of $C_2H_5C(O)CCo_3(CO)_9$.

Some attempted, but unsuccessful, decarbonylations also may be mentioned.

Attempted decarbonylation of $CH_3C(O)CCo_3(CO)_9$ in refluxing benzene solution led to complete decomposition to organic solvent—insoluble products. The same observation was made in the case of $Et_2NC(O)CCo_3(CO)_9$ and $H_2NC(O)CCo_3(CO)_9$. On the other hand, the ester $MeO_2CCCo_3(CO)_9$ was recovered in 86% yield after its benzene solution had been heated at reflux under nitrogen for 24 h.

p-$MeC_6H_4C(O)CCo_3(CO)_9$ underwent complete decomposition when heated at reflux in carbon tetrachloride solution under nitrogen (2.0 mmol in 50 mL). TLC (hexane) indicated that only decomposition was taking place and that no new soluble products were being formed. After 10 h at reflux the ketone had been consumed. The solvent was removed under reduced pressure to yield an olive green powder. No $RCCo_3(CO)_9$ complex was present.

Reduction of (Propanoylmethylidyne)tricobalt Nonacarbonyl with Trifluoroacetic Acid. A 100-mL three-necked, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser topped with a nitrogen inlet tube was purged with nitrogen and charged with 0.50 g (1.0 mmol) of $C_2H_5C(O)CCo_3(CO)_9$, 50 mL of benzene, and 1.5 mL of trifluoroacetic acid. The mixture was heated to reflux. After 75 min, TLC (CH_2Cl_2) indicated that the starting material had been consumed; only a purple compound with high R_f remained. Removal of the volatiles at reduced pressure was followed by column chromatography of the residue (silicic acid, 1:1 hexane/CH_2Cl_2). A 50% yield (0.24 g) of *n*-$C_3H_7CCo_3(CO)_9$ (identified by IR and NMR) was isolated.

A similar reaction was carried out by using 1.0 mmol of this cluster ketone, 50 mL of benzene, and 1.5 mL of CF_3CO_2D (freshly prepared from D_2O and trifluoroacetic anhydride). After 90 min at reflux, workup as above and column chromatography (Silicar CC-7, 3:1 CH_2Cl_2/hexane) followed by recrystallization from hexane gave 0.21 g (43%) of mixed $CH_3CHDCHDCCo_3(CO)_9$, $CH_3CH_2CD_2CCo_3(CO)_9$, and $CH_3CD_2CH_2CCo_3(CO)_9$ as well as other combinations. The IR spectrum of this mixture was identical with that of *n*-$C_3H_7CCo_3(CO)_9$, and structural assignment was made on the basis of the proton and deuterium NMR spectra of the mixture. The deuterium NMR spectrum indicated that there was deuterium only in the α- and the β-positions with respect to the apical carbon atom. However, the proton NMR spectrum did not match the one expected for any one of the above products but appeared to be the result of a combination of the various spectra. The proton NMR spectrum was further complicated by coupling of the deuterium atoms which, although it is small, causes broadening of the peaks.

^1H NMR ($CDCl_3$): δ 0.9–1.4 (m, 3 H, CH_3), 1.4–2.4 (m, 1 H, $Co_3CCH_2CH_2CH_3$), 3.5–4.0 (m, Co_3CCH_2, 0.83 H). ^2H NMR ($CHCl_3$): δ 1.98 (s, ca. 1 D, $Co_3CCH_2CD_2CH_3$), 3.75 (s, ca. 1 D, Co_3CCD_2), based on δ 7.24 for $CDCl_3$ (proton decoupled).

A similar reduction was carried out to about 50% completion by using 2.0 mmol of $C_2H_5C(O)CCo_3(CO)_9$ and only 0.5 mL of CF_3CO_2D in 50 mL of benzene (90-min reaction time at reflux). Workup as above gave 0.51 g of ketone and 0.20 g of reduced product. The former was almost pure $CH_3CD_2C(O)CCo_3(CO)_9$: NMR ($CDCl_3$) δ 1.30 (br s). IR (CCl_4) ν(C=O) 1636 (s), 1623 (sh) cm^{-1}.

Attempted reduction of $CH_3CD_2C(O)CCo_3(CO)_9$ (1.0 mmol) with 1 mL of CF_3CO_2D in 50 mL of benzene at reflux was unsuccessful. TLC indicated that the reduction was proceeding only very slowly. After 3 h, another 2 mL of CF_3CO_2D was added. After another 5 h at reflux, TLC showed that there was some reduction product, but a great deal of total decomposition was obvious. Workup as above gave a small quantity of reduction product which was not sufficient for characterization. Reduction of $CH_3CD_2C(O)CCo_3(CO)_9$ (1.0 mmol) with 1.5 mL of CF_3CO_2H in 50 mL of benzene at reflux (4-h reaction time), on the other hand, was successful. Workup as above gave 0.11 g (23%) *n*-butylidynetricobalt nonacarbonyl which NMR showed to be a mixture of the various combinations of α- and β-deuterated compounds.

Reduction of (Isopropenylmethylidyne)tricobalt Nonacarbonyl with Deuteriotrifluoroacetic Acid. The usual apparatus was charged with 0.48 g (1.0 mmol) of $CH_2{=}CMeCCo_3(CO)_9$,[27] 2 mL of CF_3CO_2D, and 50 mL of benzene. After this solution had been stirred and heated at reflux under nitrogen for 4 h, removal of volatiles and column chromatography of the residue gave 0.25 g (52%) of (2-methylpropylidyne)tricobalt nonacarbonyl which had an IR spectrum identical with that of an authentic sample. The proton NMR spectrum suggested that it was a mixture of the following deuterated compounds: $CH_3(CH_2D)CDCCo_3(CO)_9$, $CH_3(CHD_2)CHCCo_3(CO)_9$, and $(CH_2D)_2CHCCo_3(CO)_9$. NMR ($CDCl_3$): δ 1.35-1.7 (m, ca. 4.4 H, CH_3), 3.6-4.0 (m, 1 H, $C\mathit{H}Me_2$). The proton NMR spectrum did not match that expected for any one of the above products but appeared to represent a combination of the various deuterated products.

Reduction of (Propanoylmethylidyne)tricobalt Nonacarbonyl with Acetic Acid. The standard apparatus used in the CF_3CO_2H reductions was charged with 0.5 g (1.0 mmol) of $C_2H_5C(O)CCo_3(CO)_9$, 1.5 mL of glacial acetic acid, and 50 mL of benzene. The mixture was stirred and heated at reflux under nitrogen. After 2 h, TLC showed that all of the starting ketone had been consumed and that two products, one of higher and the other of lower R_f than the ketone, were present. The usual workup gave 0.03 g (6%) of $n\text{-}C_3H_7CCo_3(CO)_9$ and 0.29 g (58%) of $C_2H_5CH(OH)CCo_3(CO)_9$, mp 136-138 °C (lit.[6] mp 137-138 °C). Both products were identified by comparison of their IR spectra with those of authentic samples.

A similar reaction with 1.0 mmol of $Me_2CHC(O)CCo_3(CO)_9$ with 1 mL of glacial acetic acid in refluxing benzene solution for 5 h gave a very small quantity of $Me_2CHCH_2CCo_3(CO)_9$ and 0.21 g (41%) of $Me_2CHCH(OH)CCo_3(CO)_9$, mp 113-115 °C (lit.[6] mp 114-116 °C).

Dehydrogenation of (2-Hydroxyalkylidyne)tricobalt Nonacarbonyl Complexes in Refluxing Benzene. The example of (2-hydroxy-3-methylbutylidyne)tricobalt nonacarbonyl is typical.

A 100-mL three-necked flask equipped with a magnetic stir bar and a reflux condenser topped with a nitrogen inlet tube was purged with nitrogen and charged with 1.03 g (2.0 mmol) of $Me_2CHCH(OH)CCo_3(CO)_9$ and 50 mL of benzene. The solution was stirred and heated at reflux under nitrogen for 4 h, until TLC showed the absence of starting material and the presence of two products which gave purple and brown spots, respectively. Both were of higher R_f than the starting alcohol. The solvent was removed under reduced pressure, and the residue was purified by column chromatography to yield 0.10 g (10%) of $Me_2CHCCo_3(CO)_9$ and 0.54 g (53%) of $Me_2CHC(O)CCo_3(CO)_9$, mp 150-153 °C (lit.[3] mp 150-153 °C dec). Both compounds were identified by comparison of their IR spectra with those of authentic samples.

This reaction was repeated by using 0.40 g (0.78 mmol) of the alcohol in 50 mL of benzene, but 10 drops of alcoholic sodium hydroxide also were added. A 2.5-h reflux period sufficed to consume the starting material. TLC showed that a single product (brown spot) of higher R_f had been formed. Workup as above gave 0.28 g (70%) of $Me_2CHC(O)CCo_3(CO)_9$, mp 151-153 °C.

In the case of $ArCH(OH)CCo_3(CO)_9$ compounds only the decarbonylation products were obtained. When 0.55 g (1.0 mmol) of $PhCH(OH)CCo_3(CO)_9$ in 50 mL of benzene was heated at reflux under nitrogen, TLC (1:3 CH_2Cl_2/hexane) indicated that the ketone was forming but that it was decarbonylating as it was being formed. After 6 h at reflux, no starting alcohol remained. Removal of solvent was followed by column chromatography of the residue to give 0.28 g (54%) of $PhCCo_3(CO)_9$ (mp 105-106 °C), identified by comparison of its IR spectrum with that of an authentic sample.

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Metalloporphyrins with Unusual Geometries. 1. Mono-, Di-, Triatom-Bridged Porphyrin Dimers

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Abstract: The electronic structure of mono-, di-, and triatom-bridged metalloporphyrin dimers is examined to show how orbital symmetries and electron counts determine their geometries and electronic properties. An orbital diagram constructed for $(N_4M){-}X{-}(MN_4)$, where N_4 is a model porphyrin and X denotes an O, N, or C atom, accounts for the bending preference and magnetic behavior of the X = O, N species. The analysis of the diagram leads us to predict that the carbido-bridged complexes should be stable diamagnetic molecules having a linear M—C—M spine. The Walsh diagram for bending of the M—O—O bonds in $(N_4M){-}O{-}O{-}(MN_4)$ shows that geometrical preferences of M = Fe and M = Co compounds are very much alike. Although the normal trans bent M—O—O—M structure is calculated to be most stable, a cis bent alternative is also a possibility, if the steric constraints allow it. A side-on structure, which may be accessible for low d-electron counts, is at relatively high energy for d^4–d^4 metals. The simultaneous 1,2 migration of two metalloporphyrin fragments on O_2 encounters a level crossing between occupied and unoccupied valence orbitals for M = Co and Fe. Two remarkably different molecular structures of an $M_2O_3^{4+}$ unit in (O=Mo—porphyrin)—O—(porphyrin—Mo=O) and (Nb—porphyrin)—O_3—(Nb—porphyrin) can be explained by optimal M—O π interactions.

Metalloporphyrins in protein systems perform an important class of biochemical functions in nature. Hemoglobin, myoglobin, chlorophyll, cytochromes, catalase, and peroxidase are all well-known examples, the chemistry of which relates principally to redox reactions and the transport, storage, and activation of molecular oxygen. Over the years a great biochemical effort has brought us substantial understanding of the structure-function relationship in these natural metalloporphyrins.

Inorganic chemists have been very active in this field as well. They have made a large number of synthetic models for naturally occurring metalloporphyrins in their effort to determine the factors which govern the biological function of the natural porphyrins

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