Journal of Organometallic Chemistry, 134 (1977) 67—83

ORGANOCOBALT CLUSTER COMPLEXES

XXII *. α,β-UNSATURATED METHYLIDYNETRICOBALT NONACARBONYL COMPLEXES

DIETMAR SEYFERTH, C. SCOTT ESCHBACH, GARY H. WILLIAMS and PAUL L.K. HUNG
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received January 11th, 1977)

Summary

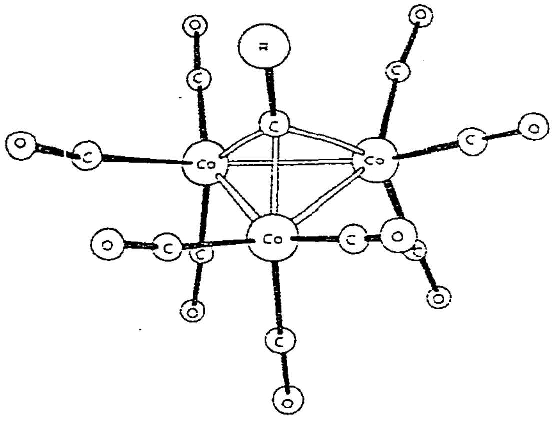
The reaction of the appropriate $RCCl_3$ compound with dicobalt octacarbonyl has been used to prepare $CH_2{=}CHCCo_3(CO)_9$, $CH_2{=}C(CH_3)CCo_3(CO)_9$, $Me_3SiCH{=}CHCCo_3(CO)_9$ and $CH_3C(O)CH{=}CHCCo_3(CO)_9$. A similar reaction with $CH_2{=}CHCH_2CCl_3$ gave a mixture of $CH_2{=}CHCH_2CCo_3(CO)_9$, $CH_3CH{=}CHCCo_3(CO)_9$ and $CH_3CH_2CH_2CCo_3(CO)_9$. Protonation of these α,β-unsaturated methylidynetricobalt nonacarbonyl complexes resulted in formation of the α-cluster carbonium ions (e.g., $CH_2{=}C(CH_3)CCo_3(CO)_9 + HPF_6 \rightarrow (OC)_9Co_3CC(CH_3)_2{}^+PF_6{}^-$), with desilylation occurring during the protonation of $Me_3SiCH{=}CHCCo_3(CO)_9$. The $CH_3C(O)Cl/AlCl_3$ reagent was used to acetylate the first two listed complexes in the β position, and methoxymercuration of $CH_2{=}CHCCo_3(CO)_9$ with $Hg(O_2CCF_3)_2$, followed by anion exchange with NaCl, gave $ClHgCH_2CH(OCH_3)CCo_3(CO)_9$.

Introduction

In our previous studies of the chemistry of alkylidynetricobalt nonacarbonyl complexes, $RCCo_3(CO)_9$, I, we concentrated on the development of the organofunctional chemistry of these complexes [3]. Of special interest was the finding that nonacarbonyltricobaltcarbon-substituted carbonium ions, $(OC)_9Co_3CCHR^+$, were highly stabilized, presumably as a result of electron donation from the cluster substituent to the electron-deficient carbon atom [4,5]. The route to such cations was based on the cluster-substituted alcohols (eq. 1). The only suc-

---

* Part XXI, ref. 1; Preliminary communication ref. 2.

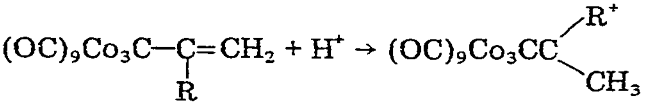


(I)

$$(OC)_9Co_3CCH(OH)R \xrightarrow[(EtCO)_2O]{HPF_6} (OC)_9Co_3CCHR^+PF_6^- \qquad (1)$$

cessful preparation of such alcohols proceeded by hydrosilylation of the respective $(OC)_9Co_3CC(O)R$ compounds (R = H, alkyl, aryl) [6], and thus we were restricted in our studies to the primary and secondary carbonium ions.

The protonation of allylidynetricobalt nonacarbonyl complexes in principle should provide an alternative route to cluster-substituted carboniom ions, including the hitherto unavailable tertiary species (eq. 2). The present study was undertaken to examine this possibility.



$$(OC)_9Co_3C{-}\underset{R}{C}{=}CH_2 + H^+ \rightarrow (OC)_9Co_3CC\begin{smallmatrix} \diagup R^+ \\ \diagdown CH_3 \end{smallmatrix} \qquad (2)$$

Results and discussion

In principle, the general route to $RCCo_3(CO)_9$ complexes (eq. 3) [7,8] should

$$RCX_3 + Co_2(CO)_8 \rightarrow RCCo_3(CO)_9 \qquad (3)$$

be applicable to the synthesis of vinyl derivatives (R = $CH_2{=}CH$, $RCH{=}CH$, $CH_2{=}C(R)$, etc.). In practise, the preparation of such compounds by this procedure was not straightforward. In contrast to the usually successful conditions for effecting $RCCo_3(CO)_9$ syntheses via reaction 3, it was of critical importance to use rigorously dried THF, water-free dicobalt octacarbonyl and a nonhydrolytic, aprotic work-up in the preparation of α,β-unsaturated cluster complexes in order to avoid contamination by the saturated complex. Also, it was found advisable to destroy any unconverted $Co_2(CO)_8$ prior to further work-up after the reaction was over. In our early studies with $CH_2{=}CHCCo_3(CO)_9$ [9] this product invariably contained minor amounts of $C_2H_5CCo_3(CO)_9$, which was detectable by NMR, and in an extreme case, our first attempted synthesis of *trans*-$Me_3SiCH=CHCCo_3(CO)_9$ gave instead the saturated compound, $Me_4SiCH_2CH_2CCo_3(CO)_9$ as sole product [10]. Separation of the saturated complexes from the α,β-unsaturated complexes could not be effected by column chromatography on silicic acid or fractional crystallization, so care must be taken to avoid their formation during the reaction and the work-up procedure. By use of the proper reaction conditions and of work-up procedures designed to destroy unreacted $Co_2(CO)_8$ and to avoid contact with acid, the desired α,β-unsaturated derivatives could be prepared free of reduced contaminants [11]. Prepared by this route were $CH_2=CHCCo_3(CO)_9$, $CH_2=C(CH_3)CCo_3(CO)_9$, *trans*-$Me_3SiCH=CHCCo_3(CO)_9$ and *trans*-$CH_3C(O)CH=CHCCo_3(CO)_9$.

Attempted preparation of 3-butenylidynetricobalt nonacarbonyl by the reaction of 1,1,1-trichloro-3-butene with dicobalt octacarbonyl using the above-mentioned conditions gave a mixture (by NMR) of the desired $CH_2=CHCH_2CCo_3(CO)_9$ (63%), $CH_3CH=CHCCo_3(CO)_9$ (27%) and $CH_3CH_2CH_2CCo_3(CO)_9$ (10%) which was not resolvable by column chromatography.

Both the isomerization reaction and the reduction reactions which were observed in these reactions of unsaturated $RCCl_3$ compounds with dicobalt octacarbonyl are indicative of the presence of cobalt tetracarbonyl hydride, $HCo(CO)_4$, during the course of the reaction and/or during the work-up procedure. The isomerization of terminal olefins to internal olefins, e.g., of $PhCH_2CH=CH_2$ to $PhCH=CHCH_3$, is a process which is known to be induced by dicobalt octacarbonyl and cobalt tetracarbonyl hydride [12]. Also, stoichiometric reactions of $HCo(CO)_4$ with various olefins under mild conditions have been reported to result in hydrogenation of the C=C bond [13]. Such observed reductions include those of styrene to ethylbenzene, α-methylstyrene to isopropylbenzene, 1-heptene to n-heptane, 1,3-cyclohexadiene to cyclohexene, allyl ethyl ether to ethyl propyl ether and various α,β-unsaturated aldehydes and ketones to the saturated carbonyl compounds. Olefin reduction also is a side reaction which occurs during the hydroformylation of olefins [13]. In general, conjugated olefins, such as phenyl-substituted ethylenes, 1,3-dienes and α,β-unsaturated carbonyl compounds are most readily hydrogenated by such stoichiometric or catalytic cobalt carbonyl systems. There is even one example of the hydrogenation of an α,β-unsaturated methylidynetricobalt nonacarbonyl derivative under hydroformylation conditions (eq. 4) [14]. In all such processes an oxidative addition-reductive elimination sequence similar to that which obtains in the hydroformylation of olefins is believed to be operative [13].

$$(OC)_9Co_3CCH=CHCO_2H \xrightarrow[Co_2(CO)_8,\ 110^\circ C]{H_2/CO\ (260\ atm.)} (OC)_9Co_3CCH_2CH_2CO_2H \qquad (4)$$

In order to show that $HCo(CO)_4$ was capable of causing the reductions which we observed, we carried out experiments in which this compound either was generated in situ in the presence of $CH_2=CHCCo_3(CO)_9$ and $CH_2=C(CH_3)CCo_3(CO)_9$ or was prepared separately and then added to the latter. Thus both of these vinylic cluster complexes were reduced to the corresponding alkyl compounds, $C_2H_5CCo_3(CO)_9$ and $Me_2CHCCo_3(CO)_9$, respectively, upon treatment with dicobalt octacarbonyl and trifluoroacetic acid in THF solution. In another experiment which was designed to approximate the conditions used in the work-up of the $CH_2=C(CH_3)CCl_3$ + $Co_2(CO)_8$ reaction mixture which had led to formation of the reduced product, $CH_2=C(CH_3)CCo_3(CO)_9$ was treated with a THF solution of $Co_2(CO)_8$ and 1 *M* hydrochloric acid. The isopropyl-substituted cluster complex was formed in 85% yield. Finally, treatment of $CH_2=C(CH_3)CCo_3(CO)_9$ with $HCo(CO)_4$ in THF under a carbon monoxide atmosphere gave $Me_2CHCCo_3(CO)_9$ in 97% yield *. It is clear that the precisely defined experimental conditions required for the successful preparation of alkenylidynetricobalt nonacarbonyl complexes free of saturated contaminants are those which avoid the adventitious formation of cobalt tetracarbonyl hydride. The hydrogenation of olefins by $HCo(CO)_4$ in the absence of hydrogen is a stoichiometric process, but the isomerization of terminal olefins by $HCo(CO)_4$ is a catalytic process [13]. Thus it is no surprise that the isomerization of $CH_2=CHCH_2CCo_3(CO)_9$ occurred even when care was taken to avoid formation of $HCo(CO)_4$; apparently catalytic amounts of this reagent were formed nevertheless.

The availability of several alkenylidynetricobalt nonacarbonyl complexes allowed us to explore their chemistry. As expected, they reacted readily with electrophilic reagents in the sense of eq. 2, with β-addition of the positively charged species to produce an α-cluster carbonium ion.

The reaction of 65% aqueous hexafluorophosphoric acid in propionic anhydride medium with alcohols of type $(OC)_9Co_3CCH(OH)R$ had proved to be a successful procedure for the preparation of stable carbonium ion salts, $(OC)_9Co_3CCHR^+PF_6^-$ [4]. This procedure could be adapted nicely to the generation of carbonium ions from the alkenylidynetricobalt nonacarbonyl complexes. Thus treatment of a benzene solution of $CH_2=C(CH_3)CCo_3(CO)_9$ with the $HPF_6/(EtCO)_2O$ reagent resulted in precipitation of the tertiary carbonium ion salt, $(OC)_9Co_3CC(CH_3)_2{}^+PF_6^-$, as a brown powdery solid. This salt reacted with nucleophiles as a carbon-electrophile, as shown in Scheme 1. The high stability of the carbonium ion makes the purification and isolation of derived products difficult. For instance, attempted purification of the methyl ether, $(OC)_9Co_3CC(CH_3)_2OCH_3$, by column chromatography using pH 4 silicic acid resulted in isolation of the alcohol instead. The methyl ether is cleaved by dilute strong acid and subsequent deprotonation regenerates $(OC)_9Co_3CC(CH_3)=CH_2$. Since H^+ is generated in the reaction of the carbonium ion with methanol, high yields of the methyl ether were obtained only by using a large excess of methanol and subsequently pouring the reaction mixture into dilute aqueous sodium bicarbonate. This carbonium ion also could be generated by dissolving the alcohol, $(OC)_9Co_3CC(CH_3)_2OH$, in concentrated sulfuric acid. When such a solution was poured onto ice, a mixture of the expected alcohol and the starting isopropenyl-substituted cluster complex was isolated. The latter was not detectable by ^1H and ^{13}C NMR spectroscopy in the sulfuric acid solution and therefore must have been formed during the hydrolysis step **.

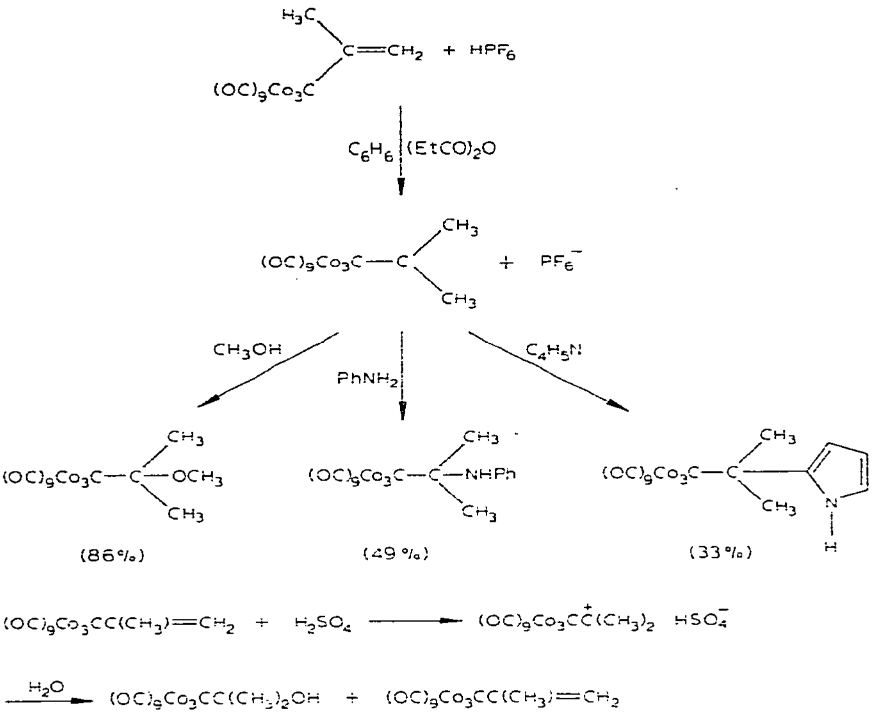
Similar reactions were carried out with $CH_2=CHCCo_3(CO)_9$. Reaction of this

---

* It should be mentioned that $CH_2=C(CH_3)CCo_3(CO)_9$ has been prepared by the reaction of dimethylketene with $Co_2(CO)_8$ and hydrogenated to $Me_2CHCCo_3(CO)_9$ using a palladium on charcoal catalyst [15].

** The ^1H and ^{13}C NMR spectra of $(OC)_9Co_3CC(CH_3)_2{}^+$ will be discussed in a later paper which will cover our other carbonium ion studies.

SCHEME 1



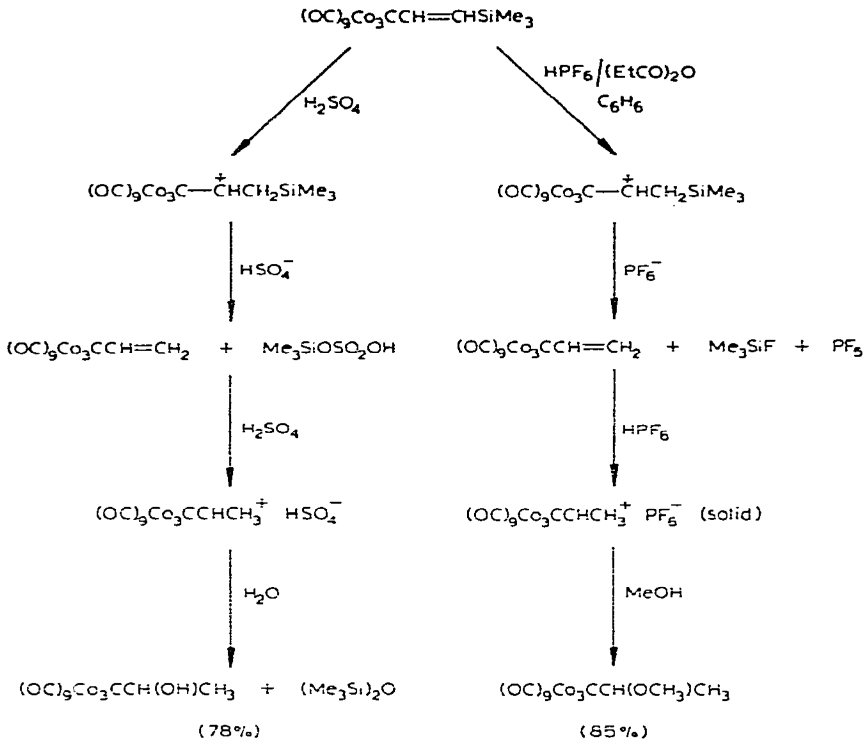
Reactions of $(OC)_9Co_3C\overset{+}{C}(CH_3)_2$

compound with $HPF_6/(EtCO)_2O$ in benzene gave a black solid which was filtered and treated with anhydrous methanol. The expected $(OC)_9Co_3CCH(OCH_3)CH_3$ was obtained in 53% yield. Solution of the vinyl-substituted cluster complex in concentrated sulfuric acid did give the carbonium ion, $(OC)_9Co_3CCHCH_3^+$, but as in the case of the isopropenyl-substituted complex, when this sulfuric acid solution was poured onto ice, a mixture of the alcohol (38%) and the vinyl-substituted cluster (34%) was formed. In terms of product yields, the $(OC)_9Co_3CCH(OH)CH_3$ + $HPF_6/(EtCO)_2O$ route to this carbonium ion and its derived products [4] is much better.

The silylated cluster complex, $(OC)_9Co_3CCH{=}CHSiMe_3$, underwent protonation and desilylation on treatment with $HPF_6/(EtCO)_2O$ or concentrated sulfuric acid, as shown in Scheme 2. That the desilylation occurred in the acid medium, not later during work-up, was shown by the proton NMR spectrum of a solution obtained by dissolving $(OC)_9Co_3CCH{=}CHSiMe_3$ in concentrated sulfuric acid. The NMR spectrum of the known $(OC)_9Co_3CCHCH_3^+$ was clearly discernible. Such elimination of an olefin from a carbonium ion in which the charged center is β to a silyl group is a well-known, general process in organosilicon chemistry [16], and its occurrence in the present instance serves to prove that the direction of proton addition to $(OC)_9Co_3CCH{=}CHSiMe_3$ proceeded as indicated in Scheme 2.

Treatment of $(OC)_9Co_3CCH{=}CHC(O)CH_3$ with concentrated sulfuric acid gave a solution of the expected carbonium ion. When this solution was poured

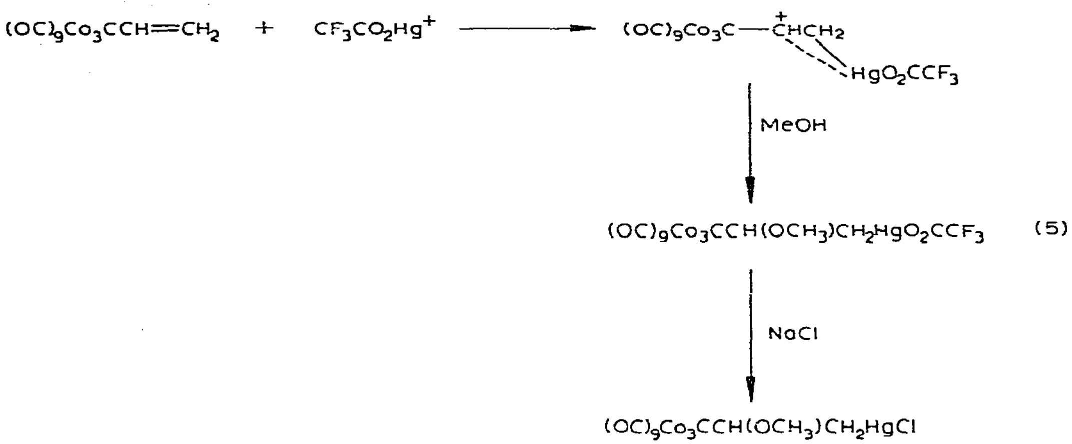
SCHEME 2



onto ice, the expected alcohol, $(OC)_9Co_3CCH(OH)CH_2C(O)CH_3$ was obtained in 12% yield, but the major product was the starting unsaturated cluster complex.

The electrophilic acetylation of such α,β-unsaturated cluster complexes proceeded less satisfactorily than their protonation. Addition of an excess of a 1 : 1 $CH_3COCl/AlCl_3$ mixture in dichloromethane to $CH_2{=}C(CH_3)CCo_3(CO)_9$, followed by hydrolysis of the reaction mixture, gace $(OC)_9Co_3CCH(CH_3)CH_2C(O)CH_3$ in 10% yield. This product is derivable from the carbonium ion formed by β-addition of CH_3CO^+ to the isopropenyl group, follwed by reduction. A similar reaction of $CH_3COCl/AlCl_3$ with $CH_2{=}CHCCo_3(CO)_9$ gave a mixture of $(OC)_9Co_3CCH_2CH_2C(O)CH_3$ (13%), $(OC)_9Co_3CCH{=}CHC(O)CH_3$ (*trans* isomer) (12%) and $(OC)_9Co_3CCH(OH)CH_2C(O)CH_3$ (6%) after hydrolysis of the reaction mixture. All three products are derivable from the initially formed $(OC)_9Co_3CCHCH_2C(O)CH_3{}^+$ via reduction, deprotonation and hydrolysis, respectively. Although the product yields in these reactions are low, the product structures confirm the formation of the expected α-cluster carbonium ion. A possible explanation of the low yields obtained involves competitive interaction of aluminum chloride with the $(OC)_9Co_3C$ moiety, very likely at a carbon monoxide ligand, leading to deactivation of vinylic group, or, since none of the unsaturated cluster complex was recovered in these reactions, to destruction of the latter. In previous work we have obtained indications that some $RCCo_3(CO)_9$ are not stable to aluminum chloride [17,18].

The oxymercuration of olefins is another reaction which involves electrophilic attack at a C=C bond. The methoxymercuration of $CH_2{=}CHCCo_3(CO)_9$ with mercuric trifluoroacetate proceeded in the direction expected (eq. 5).



(5)

Again, the charged immediate is the one in which the positive charge is concentrated at the carbon atom α to the cluster.

We may conclude that this study, although limited in scope, has been useful in the further development of the chemistry of alkylidynetricobalt nonacarbonyl complexes. It has delineated the conditions required for the successful preparation of α,β-unsaturated alkylidynetricobalt nonacarbonyls and has demonstrated their potentially useful reactions with electrophilic substrates. Their main value lies in their use as precursors to tertiary cobalt cluster-substituted carbonium ions of type $(OC)_9Co_3CCRR'^+$ in the case of α-substituted α,β-unsaturated methylidynetricobalt nonacarbonyl complexes.

Experimental

General comments

Unless otherwise indicated, reactions were carried out in an apparatus which was evacuated, flame dried and refilled with nitrogen. All reactions were carried out under an atmosphere of either nitrogen or carbon monoxide. Solvents were of reagent grade quality. Tetrahydrofuran and benzene were distilled from sodium-benzophenone ketyl prior to use, stored in sealed bottles under nitrogen and transferred via syringe or cannula. Dichloromethane was used without further purification. Technical grade propionic anhydride was distilled prior to use and stored in sealed bottles under nitrogen.

The progress of reactions was often followed by color changes and was always monitored by thin layer chromatography (TLC) on Eastman Chromatogram Sheet No. 6061. The strips were eluted with hexane, dichloromethane or diethyl ether. Products were routinely isolated from reaction mixtures by separation using column chromatography.

Due to the instability of many of the derivatives towards acidic conditions it was found necessary to use pH 7 silicic acid (Mallinckrodt Silicar CC7, Special for Chromatography) for chromatographic separations. Preparative TLC plates were prepared by coating 20 cm × 20 cm glass plates with a slurry of 45 g of silica Gel GF (Sigma Chem. Co.) and 95 g of water, allowing them to dry at room temperature for several hours and baking them in an 80° C oven overnight. After developing the plates, the products were isolated by scraping the band from the plate and washing the compound from the silica with methanol or diethyl ether.

Samples recovered from chromatographic separations are reported in the order in which they eluted.

Samples were further purified by sublimation in vacuo (50—60° C/0.1 mmHg) or by recrystallization, then removal of the solvents in vacuo at room temperature.

Purification of the unsaturated derivatives by vacuum sublimation without a prior acidic work-up results in an extremely pyrophoric residue, and care should be taken when opening the sublimation apparatus.

Melting points were obtained using a Büchi circulating oil melting point apparatus, are reported in degrees Centrigrade and are uncorrected.

IR spectra were recorded in solution using 0.1 mm sodium chloride cavity cells on a Perkin—Elmer Model 337, 237B, 257 or 457A spectrophotometer. Absorptions are reported in reciprocal centimeters (cm^{-1}) and are calibrated using the 1601 cm^{-1} absorption of polystyrene.

Proton nuclear magnetic resonance spectra were recorded on a Varian Associates T-60, Perkin—Elmer Model R-20 or R-22 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, δ.

Preparation of α,β-unsaturated methylidynetricobalt nonacarbonyl complexes

(a) Allylidynetricobalt nonacarbonyl, $CH_2{=}CHCCo_3(CO)_9$. A one-liter, three-necked flask, which was equipped with a mechanical stirrer and a nitrogen inlet, was charged with 33.7 g (0.099 mol) of dicobalt octacarbonyl in 450 ml of freshly distilled THF (under nitrogen). To this solution was added by syringe 8.53 g (0.055 mol) of 3,3,3-trichloropropene [19] and the mixture was stirred at 35—40° C for 4 h., at which time no further gas evolution was observed. The mixture was allowed to cool to room temperature and subsequently the solvents wer were removed under reduced pressure. The residue was extracted thoroughly with pentane and the extracts were filtered through Celite. The pentane was removed at reduced pressure and the residue was extracted again with pentane. The extracts were filtered and evaporated at reduced pressure. The residue sublimed in vacuum at 50° C to yield 12.30 g (45%) of the purple title compound, m.p. 144—145° C (dec.). (Found, C, 30.59; H, 0.75. $C_{12}H_3O_9Co_3$ calcd.: C, 30.80; H, 0.65%). IR (CCl_4, cm^{-1}): 3080w, 3005w, 2976w, 2928w, 2510w, 2472w, 1801w, 1398m, 1273vw, 1162m, 1004m, 961m, 905s, 769s, 660s. Terminal CO region: 2100s, 2023vs, 1956(sh). NMR (CCl_4): δ 5.18—5.60 (m, 2H) and 7.45—7.94 ppm (m, 1H). That none of the saturated complex was present was shown by the absence of signals at δ 1.57 and 3.80 ppm characteristic of $CH_3CH_2CCo_3(CO)_9$.

(b) 2-Methylallylidynetricobalt nonacarbonyl, $CH_2{=}C(CH_3)CCo_3(CO)_9$. A 500 ml, three-necked flask equipped as described above was charged with 18.2 g (0.053 mol) of $Co_2(CO)_8$ in 250 ml of THF, and 4.65 g (0.029 mol) of $CCl_3C(CH_3){=}CH_2$ [20] was added. The mixture was stirred for 1 h. at room temperature, during which time no gas evolution was observed. The reation mixture then was heated at 35—40° C for 4 h. Subsequently, it was allowed to cool to

room temperature, evaporated at reduced pressure and extracted with hexane. The hexane extracts were filtered through Celite and evaporated and the extraction procedure was repeated. The purple-brown solid which was obtained was sublimed in vacuum at 50°C to give 8.36 g (59%) of the title complex, m.p. 170—173°C (dec.). (Found: C, 32.46; H, 1.11. $C_{13}H_5Co_3O_9$ calcd.: C, 32.39; H, 1.05%). IR (CCl_4, cm^{-1}): 3092w, 3000(sh), 2980w, 2960(sh), 2921w, 2519w, 2480w, 1774vw, 1451m, 1436m, 1392w, 1371m, 1043s, 891s, 712m, 671s, 592s. Terminal CO region: 2101s, 2055vs, 2043vs, 2021vs, 1980m. NMR (CCl_4): δ 2.37 (s, 3H, CH_3) and 5.17—5.38 ppm (m, 2H).

(c) trans-3-Trimethylsilylallylidynetricobalt nonacarbonyl, $Me_3SiCH=CHCCo_3(CO)_9$. A 500 ml, three-necked flask equipped as described above was charged with 16.6 g (0.049 mol) of $Co_2(CO)_8$ in 250 ml of dry THF and 9.46 g (0.027 mol) of $Me_3SiCH=CHCBr_3$ [21]. The reaction mixture was stirred at room temperature for 1 h., at 35—40°C for 3 h. and at 50°C for another 2 h. Further work-up followed the procedure described above. The final residue, a brown oil, solidified on standing and was sublimed in vacuum at 50—55°C to give 4.06 g (28%) of the title compound, m.p. 53—54°C, a purple-red solid. Yields as high as 48% can be obtained by this procedure. (Found: C, 33.29; H, 2.25. $C_{15}H_{11}O_9SiCo_3$ calcd.: C, 33.35; H, 2.05%). IR (CCl_4, cm^{-1}): 2959m, 2898w, 2520w, 2480vw, 1428w, 1402w, 1262w, 1250m, 1190m, 1168m, 1114w, 964m, 862s, 842s, 692w, 648m. Terminal CO region: 2100s, 2050vs, 2038vs, 2020s, 1950w. NMR ($CDCl_3$): δ 0.15 (s, 9H, Me_3Si), 6.03 (d, $J = 18$ Hz, 1H, $=CHSi$) and 7.73 ppm (d, $J = 18$ Hz, 1H, $=CHCCo$).

In an initial reaction, in which strictly anhydrous conditions were not ensured, the product was $Me_3SiCH_2CH_2CCo_3(CO)_9$, a purple-black solid, m.p. 64°C, in 38% yield. (Found: C, 33.18; H, 2.40. $C_{15}H_{13}O_9SiCo_3$ calcd.: C, 33.22; H, 2.41%). NMR (CCl_4): δ 0.1 (s, 9H, Me_3Si), 1.1 (t, $J = 8$ Hz, 2H, CH_2Si) and 3.5 ppm (t, $J = 8$ Hz, 2H, CH_2CCo).

(d) 3-Acetylallylidynetricobalt nonacarbonyl, $CH_3C(O)CH=CHCCo_3(CO)_9$. A 500 ml, three-necked flask equipped as described above was charged with 24.8 g (0.072 mol) of freshly sublimed dicobalt octacarbonyl * in 250 ml of dry THF and 7.48 g (0.04 mol) of $CCl_3CH=CHC(O)CH_3$ [22] was added. The mixture was stirred under nitrogen at room temperature for 90 min and then at 50°C for 2.5 h. After gas evolution had ceased, the reaction mixture was allowed to cool to room temperature. The solvent was removed at reduced pressure and the residue was extracted with diethyl ether. The extracts were filtered and evaporated and the residue was extracted again with benzene. The oily residue remaining after removal of the benzene was recrystallized from hexane to give 3.81 g (19%) of black platelets, m.p. 105—107°C (lit. [9] m.p. 107—109°C).

(e) Reaction of 1,1,1-trichloro-3-butene with dicobalt octacarbonyl. A reaction was carried out as described above using 21.4 g (0.062 mol) of dicobalt octacarbonyl in 250 ml of dry THF and 5.25 g (0.035 mol) of $CH_2=CHCH_2CCl_3$ [23] for 1 h at room temperature, 35—40°C for 4 h and 50—55°C overnight. Work-up as above followed by sublimation at 50°C in vacuum gave 5.32 g of a mixture whose complex NMR spectrum was consistent with the presence of a

---

* It is essential to sublime the $Co_2(CO)_8$ which is prepared in a water-containing system and is not supplied as anhydrous material. If this is not done, even if carefully dried THF is used, the product is the saturated complex, $CH_3C(O)CH_2CH_2CCo_3(CO)_9$.

6.3 : 2.7 : 1 mixture of $CH_2=CHCH_2CCo_3(CO)_9$, $CH_3CH=CHCCo_3(CO)_9$ and $CH_3CH_2CH_2CCo_3(CO)_9$. This mixture was not resolvable by column chromatography.

A portion of this mixture, 4.53 g, was stirred under nitrogen with 75 ml of concentrated sulfuric acid for 3 h. At this time not all of the material had dissolved. The mixture was poured onto ice and subsequently was extracted with 300 ml of diethyl ether. The organic layer was washed with water and dried. Removal of the solvent was followed by filtration chromatography (Woelm Neutral Alumina, Grade IV, hexane) to give 1.50 g of a 2.5 : 0.9 : 1 (by NMR) mixture of the above-mentioned products. Elution with benzene, followed by recrystallization from pentane, gave 1.44 g of purple $C_2H_5CH(OH)CCo_3(CO)_9$, m.p. 133—134°C (dec.) (lit. [6] m.p. 137—138°C), whose IR and NMR spectra were identical with those of an authentic sample.

Preparation of allylidynetricobalt octacarbonyltriphenylphosphine, $CH_2=CHCCo_3(CO)_8PPh_3$

A solution of 3.43 g (7.32 mmol) of $CH_2=CHCCo_3(CO)_9$ and 1.92 g (7.32 mmol) of triphenylphosphine in 150 ml of dichloromethane was stirred under nitrogen for 2 h at room temperature until TLC showed that the starting cobalt complex had been consumed. The solvent was removed and the oily brown solid residue was recrystallized from pentane to give 3.05 g (60%) of brown-black plates which decomposed slowly above 90°C and rapidly at 106—107°C. (Found: C, 49.64; H, 2.74. $C_{29}H_{18}O_3PCo_3$ calcd.: C, 49.60; H, 2.59). IR (CCl_4, cm^{-1}, terminal CO region): 2083s, 2041vs, 2030vs, 2021vs, 1992s, 1966m. NMR ($CDCl_3$): δ 5.00—5.42 (m, 3H) and 7.18—7.76 ppm (m, 15H).

Reduction of α,β-unsaturated methylidynetricobalt nonacarbonyl complexes

(a) With $Co_2(CO)_8/CF_3CO_2H$. To a magnetically stirred solution of 2.13 g (6.2 mmol) of dicobalt octacarbonyl in 40 ml of dry THF was added quickly, under a positive nitrogen flow, 0.94 g (2.0 mmol) of $CH_2=CHCCo_3(CO)_9$. Upon subsequent addition of 2.0 ml of trifluoroacetic acid a vigorous evolution of gas occurred. Stirring was continued for 45 min. The mixture was poured onto ice and extracted with hexane. The extracts were washed several times with dilute HCl, dried, and the solvents were removed at reduced pressure. Column chromatography (silicic acid/hexane) of the residue afforded 0.47 g (50%) of a single compound, $C_2H_5CCo_3(CO)_9$, m.p. 192—194°C (lit. [6] m.p. 190—192°C), whose IR and NMR spectra were identical with those of an authentic sample [6].

A similar reaction was carried out with 2.5 mmol of $Co_2(CO)_8$, 2.0 mmol of $CH_2=C(CH_3)CCo_3(CO)_9$ and 4.8 mmol of CF_3CO_2H (added at 0°C) in 25 ml of THF. Sublimation at 50°C in vacuo gave 0.87 g of a mixture of $Me_2CHCCo_3(CO)_9$ and $CH_2=C(CH_3)CCo_3(CO)_9$ in 9 : 1 ratio by NMR.

(b) With $Co_2(CO)_8$/aqueous HCl. A solution of 2.5 mmol of $Co_2(CO)_8$ and 2.0 mmol of $CH_2=C(CH_3)CCo_3(CO)_9$ in 50 ml of THF was treated with 5 ml of 1 *M* HCl, with stirring under nitrogen, for 4 h. The resulting purple solution was poured into 200 ml of water and extracted with hexane. The organic layer was dried and evaporated at reduced pressure. Sublimation of the residue at 50°C in vacuum gave 0.82 g (85%) of $Me_2CHCCo_3(CO)_9$ which decomposed above

100° C without melting and whose IR and NMR spectra were identical to those of an authentic sample [24].

(c) With $HCo(CO)_4$. Cobalt tetracarbonyl hydride was prepared from 3.0 g (8.8 mmol) of $Co_2(CO)_8$, 20 ml of pyridine and 25 ml of concentrated H_2SO_4 by the method of Sternberg et al. [25] and condensed into a 100 ml, three-necked flask which was equipped with gas inlet and outlet tubes and a no-air stopper and contained 0.97 g (2.0 mmol) of $CH_2{=}C(CH_3)CCo_3(CO)_9$ cooled to about −78° C. After all of the $HCo(CO)_4$ had condensed, 25 ml of dry THF which had been cooled to −78° C was added by cannula. The mixture was maintained at −78° C for 1 h. under a carbon monoxide atmosphere and then was allowed to warm in an ice bath over a period of 2 h. Subsequently, it was allowed to come to room temperature (still under CO). The flask then was flushed with nitrogen and the solvent was removed at reduced pressure. The residue was sublimed at 45° C in vacuum to give 0.94 g (97%) of $Me_2CHCCo_3(CO)_9$.

Protonation of α,β-unsaturated methylidynetricobalt nonacarbonyl complexes. Reactions of carbonium ion salts

The standard cation formation apparatus consisted of a 200 ml round bottomed flask, modified by the attachment of a straight 30 mm glass tube with a coarse glass frit and 19/38 standard taper joint colinear with the neck of the flask. A 24/40 standard taper joint was attached at an angle of 45° to the neck. The apparatus was equipped with a nitrogen inlet, no air stopper and a 100 ml, three-necked flask with a nitrogen inlet and glass stopper attached below the glass frit. When the apparatus contained solutions it was necessary to force nitrogen upward through the frit in order to prevent the solution from filtering. During filtration nitrogen was forced down through the frit and the filtrate collected in the three-necked flask. The flask was removed, the reaction apparatus capped and the solid was dried in vacuo.

(a) 2-Methylallylidynetricobalt nonacarbonyl. The standard apparatus for cation formation was charged with 0.97 g (2.0 mmol) of $CH_2{=}C(CH_3)CCo_3(CO)_9$, 50 ml of dry benzene, 5 ml of propionic anhydride, and treated with 0.5 ml of 65% aqueous hexafluorophosphoric acid. After the mixture had been stirred for 30 min, a black solid was present, the mixture was filtered and the residue was washed with two 10 ml portions of dry benzene to give dimethylcarbonium-methylidynetricobalt nonacarbonyl hexafluorophosphate as a brown, powdery solid. To this solid was added 10 ml of absolute methanol, and the slurry was stirred for 10 min, then filtered into a solution of 5 g of sodium bicarbonate in 100 ml of water. The residue was washed with an additional 10 ml of absolute methanol and filtered into the aqueous mixture. The residue was then dissolved in hexane and also filtered into the aqueous mixture. The layers were separated and the aqueous layer back extracted with hexane. The organic layers were combined, dried over magnesium sulfate, and the solvents were removed under reduced pressure. The residue was sublimed in vacuo at 50° C to yield 0.89 g (86%) of a purple-black solid identified as 2-methoxy-2-methylpropylidynetricobalt nonacarbonyl, which does not melt, but smokes and decomposes when heated rapidly to temperatures above 200° C. (Found: C, 32.84; H, 1.80. $C_{14}H_9O_{10}Co_3$ calcd.: C, 32.71; H, 1.77%). IR (CCl_4, cm^{-1}, terminal CO region): 2100s, 2058vs, 2042vs, 2023vs and 1943s. NMR (CCl_4): δ 1.70 (s, 6H) and 3.40 ppm (s, 3H).

The reaction conditions and work-up procedure for this reaction are critical. Attempted isolation of the product by other procedures resulted in isolation of impure or different products. Attempted purification by column chromatography on silicic acid resulted in isolation of 2-hydroxy-2-methylpropylidynetricobalt nonacarbonyl. Dissolution of the carbonium ion salt in nitromethane before addition of methanol and attempted purification by column chromatography using Woelm Neutral Alumina Grade IV resulted in isolation of a mixture of 2-methylallylidynetricobalt nonacarbonyl, 2-methylpropylidynetricobalt nonacarbonyl, and the desired ether. Addition of absolute methanol to a slurry of the carbonium ion in hexane resulted in isolation of a mixture of isopropenylmethylidynetricobalt nonacarbonyl and the desired ether. Although separation of these two compounds was accomplished by column chromatography using Silicar CC-7 (pH 7) silicic acid, the yield of the ether was low.

In another experiment, a slurry of $(OC)_9Co_3CC(CH_3)_2{}^+PF_6{}^-$ was prepared as above from 2.0 mmol of 2-methylallylidynetricobalt nonacarbonyl in 20 ml of benzene. To the slurry was added via syringe 0.57 g (5.5 mmol) of aniline (previously distilled and stored over Linde Molecular Sieves 4A). After stirring for 15 min the mixture was filtered into 100 ml of water. The layers were separated, and the organic layer was dried over magnesium sulfate. The solvents were removed under reduced pressure to give 1.02 g (73%) of crude solid, m.p. 79—80°C (dec.), whose NMR spectrum was consistent with 2-anilino-2-methylpropylidynetricobalt nonacarbonyl. Recrystallization from pentane afforded 0.58 g (49%) of a brown solid identified as the above amine, m.p. 101—102°C (dec.). (Found: C, 39.45; H, 2.26; N, 2.35. $C_{19}H_{12}Co_3O_9N$ calcd.: C, 39.68; H, 2.11; N, 2.44%). IR (CCl_4, cm^{-1}, terminal CO region): 2099s, 2051vs, 2040vs, 2005s. NMR ($CDCl_3$): δ 1.75 (s, 6H, CH_3), 3.40 (br, 1H, NH) and 7.15 ppm (m, 5H, Ph).

This amine is very sensitive to chromatography and all attempts to purify it by use of column chromatography or preparative TLC caused decomposition or isolation of a different product. Attempted purification on Silicar CC-7 (pH 7) silicic acid resulted in hydrolysis to 2-hydroxy-2-methylpropylidyne tricobalt nonacarbonyl. Column chromatography using Woelm Neutral Alumina Activity Grade IV resulted in isolation of a mixture of isopropenylmethylidynetricobalt nonacarbonyl and 2-methylpropylidynetricobalt nonacarbonyl and extensive decomposition. An attempt in which preparative TLC plates prepared from Silica Gel G.F. (Sigma Chem. Co.) were used gave only 2-hydroxy-2-methylpropylidynetricobalt nonacarbonyl (30%) and extensive decomposition.

A reaction of $(OC)_9Co_3CC(CH_3)_2{}^+PF_6{}^-$ with pyrrole was carried out as well. A sample of this salt was prepared as before from 0.97 g (2.0 mmol) of 2-methylallylidynetricobalt nonacarbonyl and slurried in 20 ml dry benzene. To the slurry was added via syringe 0.70 g (10.5 mmol) of pyrrole. After it had been stirred under a nitrogen atmosphere for 1 h the mixture became homogeneous and was poured into 200 ml of water. The layers were separated, and the organic layer dried over magnesium sulfate. The solvents were removed under reduced pressure. The residue was separated by dry column chromatography (Woelm Neutral Alumina Activity Grade IV) by first eluting with hexane to remove a minor component, which was discarded; then eluting with benzene to give a brown solid, which was sublimed in vacuo at 55°C to give 0.38 g

(33%) of 2-(2-pyrrolyl)-2-methylpropylidynetricobalt nonacarbonyl, $(OC)_9Co_3CC(CH_3)_2$-2-C_4H_4N, m.p. 195—197° C. (Found: C, 37.47; H, 1.98; N, 2.49. $C_{17}H_{10}NO_9Co_3$ calcd.: C, 37.18; H, 1.84; N, 2.55%). IR (CCl_4, cm^{-1}, terminal CO region): 2100s, 2057vs, 2047vs, 2025s, 1967(sh). NMR (CCl_4): δ 1.90 (s, 6H, CH_3), 6.02 and 6.56 (m, 3H, aromatic) and 7.85 ppm (br, 1H, NH).

The alcohol, 2-hydroxy-2-methylpropylidynetricobalt nonacarbonyl, was prepared from the carbonium ion bisulfate by the following procedure.

A 200 ml three-necked flask, equipped with a nitrogen inlet, was flushed with nitrogen, charged with 1.00 g (2.06 mmol) of 2-methylallylidynetricobalt nonacarbonyl and 20 ml of concentrated sulfuric acid was added under a positive flow of nitrogen. After it had been stirred for 30 min, the brown homogeneous solution was poured into 200 ml of a well-stirred ice/water slush. The mixture was extracted with dichloromethane, the layers separated and the aqueous layer back extracted with dichloromethane. The combined organic layers layers were washed once with 5% aqueous sodium bicarbonate solution, once with water and dried over magnesium sulfate. After removal of the solvents under reduced pressure, the residue was filtered through a layer of silicic acid with hexane to elute, after removal of hexane and sublimation in vacuo at 50° C, 0.33 g (33%) of 2-methylallylidynetricobalt nonacarbonyl, m.p. 170—173°C, whose IR spectrum was identical to that of an authentic sample. The silicic acid was washed with dichloromethane to elute, after removal of the solvent and recrystallization from pentane, 0.54 g (52%) of a black solid, identified as the compound $(OC)_9Co_3CC(CH_3)_2OH$, which decomposes without melting when warmed above 50°C.(Found: C, 31.21; H, 1.58. $C_{13}H_7O_{10}Co_3$ calcd.: C, 31.22; H, 1.41%). IR (CCl_4, cm^{-1}, terminal CO region): 2100m, 2058s, 2045s, 2030(sh), 1950m. NMR ($CDCl_3$): δ 1.77 (s, 6H, CH_3) and 2.08 ppm (s, 1H, OH).

(b) Allylidynetricobalt nonacarbonyl. The standard apparatus for cation formation was charged with 50 ml dry, distilled benzene, 3.0 ml propionic anhydride, and 0.94 g (2.0 mmol) of allylidynetricobalt nonacarbonyl and stirred to effect solution. To this purple solution was added 0.5 ml of 65% aqueous hexafluorophosphoric acid. After it had been stirred for 15 min the mixture was filtered to give a black solid. The solid was washed with 10 ml of dry benzene and filtered to give a colorless filtrate. To the solid was added via a syringe 10 ml of absolute methanol and the slurry stirred for 5 min, then filtered into a solution of 5 g of sodium bicarbonate in 100 ml of water. A second 10 ml of absolute methanol was added to the remaining solid and again filtered into the aqueous mixture. The residue was dissolved in hexane and also added to the aqueous mixture. The layers were separated; the aqueous layer was back-extracted with hexane, and the combined hexane layers were dried over magnesium sulfate. After removal of the solvent under reduced pressure, the residue was sublimed in vacuo at 50—55° C to give 0.53 g (53%) of 2-methoxy-propylidynetricobalt nonacarbonyl, m.p. 175—176° C (lit. [4], 176—177° C), whose NMR spectrum was identical to that of an authentic sample.

In another experiment, a 500 ml, three-necked flask which was equipped with a nitrogen inlet and a magnetic stirring unit, was charged with 1.14 g (2.45 mmol) of allylidynetricobalt nonacarbonyl and 400 ml of concentrated sulfuric acid which had been chilled to 0° C. The flask was immersed in an ice/water bath and the mixture was stirred for 20 min. The resulting brown solution was poured slowly into a well-stirred ice/water mixture. The organic product was extracted with diethyl ether. The extracts were dried and evaporated at reduced pressure. The residue was chromatographed on silicic acid with hexane, followed by dichloromethane to give two cluster complexes. The first was sublimed to give 0.38 g (34% by weight) of a purple solid which IR and NMR analysis showed to be a mixture of $C_2H_5CCo_3(CO)_9$ and $CH_2{=}CHCCo_3(CO)_9$ in 1 : 1.7 ratio. The second compound to elute was recrystallized from pentane to give 0.45 g (38%) of $CH_3CH(OH)CCo_3(CO)_9$, m.p. 159—160°C (Lit. [6] m.p. 160—161°C), whose IR and NMR spectra were identical to those of an authentic sample [6].

(c) 3-Trimethylsilylallylidynetricobalt nonacarbonyl. A 100 ml three-necked flask with gas inlet tube was charged with 50 ml of concentrated sulfuric acid and degassed by two freeze-thaw cycles. The flask was fitted with a thermometer and cooled to 0°C in an ice/water bath. To the cold sulfuric acid was added with stirring under a positive nitrogen flow 1.95 g (3.6 mmol) of 3-trimethylsilylallylidynetricobalt nonacarbonyl. The temperature rose to 5°C, then returned to 0°C and the mixture was stirred for an additional 2 h. The brown mixture was allowed to warm to room temperature, stirred for an additional 2 h, and poured into 500 ml of a well stirred ice/water mixture. The mixture was extracted thoroughly with 350 ml of diethyl ether. The layers were separated, the organic layer washed with water, dried over magnesium sulfate, filtered and trap-to-trap distilled (0.05 mm, room temperature, closed system). The non-volatile residue was recrystallized from pentane to give 1.36 g (78%) of black plates, identified as 2-hydroxypropylidynetricobalt nonacarbonyl, m.p. 158—160°C (lit. [6] 160—162°C), by comparison of its IR spectrum to that of an authentic sample. The volatiles from the trap-to-trap distillation were concentrated to about 10 ml by distillation through a 6″ Vigreux column and subjected to GLC analysis (4 ft × 0.25 in 10% UC-W98 silicone rubber at 65°C, octane internal standard) to give 0.105 g (36%) of hexamethyldisiloxane, whose IR and NMR spectra were identical to those of an authentic sample.

Another experiment was carried out using the $HPF_6/(EtCO)_2O$ procedure. The standard cation formation apparatus was charged with 1.06 g (1.95 mmol) of 3-trimethylsilylallylidynetricobalt nonacarbonyl in 50 ml of benzene and 5 ml of propionic anhydride. To this solution was added 0.5 ml of 65% aqueous hexafluorophosphoric acid. After it had been stirred for 20 min, the mixture was filtered under nitrogen to leave a black solid, which was washed with an additional 10 ml of benzene. Addition of 10 ml of absolute methanol and stirring for 15 min gave a purple slurry, which was filtered into 100 ml of water containing 5 g of sodium bicarbonate. The residue was washed with an additional 10 ml of absolute methanol, and filtered into the aqueous mixture. The remaining solid was dissolved in pentane and also filtered into the mixture. The layers were separated, and the aqueous layer was re-extracted with pentane. The combined organic layers were dried over sodium sulfate, and the solvents were removed under reduced pressure. The residue was sublimed in vacuo at 50°C to give 0.82 g (85%) of 2-methoxymethylidynetricobalt nonacarbonyl, m.p. 176—177°C (lit. [4] 176—177°C), identified by comparison of its IR spectrum to that of an authentic sample.

(d) 3-Acetylallylidynetricobalt nonacarbonyl. A 100 ml three-necked flask,

equipped with a nitrogen inlet, was flused with nitrogen and charged with 50 ml of concentrated sulfuric acid. After the flask had been cooled in an ice bath, 1.26 g (2.47 mmol) of 3-acetylallylidynetricobalt nonacarbonyl was added quickly. The mixture was stirred for 20 min, and then the ice bath was removed. The mixture was stirred at room temperature under a nitrogen atmosphere for an additional hour. The homogeneous brown solution was poured onto ice, extracted with diethyl ether, and the layers were separated. The ether layer was washed with water and dried over magnesium sulfate. The solvents were removed under reduced pressure, and the products were separated by column chromatography (Silicar CC-7/benzene). The first compound eluted as a minor purple band and was discarded. The second compound to elute was recrystallized from pentane to give 0.65 g (52%) of the starting olefin as brown platelets, m.p. 106—107° C (dec.), identified by comparison of its IR spectrum to that of an authentic sample. The last band to elute was recrystallized from pentane to give 0.15 g (12%) of 2-hydroxy-3-acetylpropylidynetricobalt nonacarbonyl, $(OC)_9Co_3CCH(OH)CH_2C(O)CH_3$, m.p. 109—111° C (dec.). The characterization of this product will be described in the experiment below.

Acetylation of α,β-unsaturated methylidynetricobalt nonacarbonyl complexes

(a) Allylidynetricobalt nonacarbonyl. A 200 ml, three-necked flask which was equipped with a gas inlet tube and a magnetic stirring unit was charged with 1.04 g (7.8 mmol) of aluminum chloride, 50 ml of dichloromethane and 0.30 g (3.8 mmol) of acetyl chloride. Carbon monoxide was bubbled into the solution for 5 min and then 0.92 g (1.97 mmol) of allylidynetricobalt nonacarbonyl in 50 ml of dichloromethane was added. After the mixture had been stirred with carbon monoxide bubbling through it for 5 min, it was poured into water. The organic layer was separated, dried and evaporated at reduced pressure. The residue was chromatographed (silicic acid/hexane-dichloromethane). The first compound to elute was recrystallized from pentane to give 0.135 g (13%) of black needles, identified as 3-acetylpropylidynetricobalt nonacarbonyl, $CH_3C(O)CH_2CH_2CCo_3(CO)_9$, m.p. 73—74° C. (Found: C, 32.99; H, 1.57. $C_{14}H_7O_{10}Co_3$ calcd.: C, 32.84; H, 1.38%). IR ($CHCl_3$, cm^{-1}, terminal CO region): 2103vs, 2018vs, 1975(sh); ν(C=O) 1715 cm^{-1}. NMR ($CDCl_3$, CH_2Cl_2): δ 2.23 (s, 3H, CH_3), 2.96 (t, J = 7 Hz, 2H) and 3.99 ppm (t, J = 7 Hz, 2H). The second compound to elute was recrystallized from pentane, giving 0.12 g (12%) of black needles, identified as *trans*-3-acetylallylidynetricobalt nonacarbonyl, m.p. 107—109° C. (Found: C, 33.14; H, 1.13. $C_{14}H_5O_{10}Co_3$ calcd.: C, 32.97; H, 0.99%). IR ($CHCl_3$, cm^{-1}): terminal CO region, 2103vs, 2021vs, 1985(sh); ν(C=O) 1667. NMR ($CDCl_3$): δ 2.20 (s, 3H, CH_3), 6.23 (d, J = 15 Hz, 1H, =CH) and 8.33 (d, J = 15 Hz, 1H, =CH). The third compound to elute was recrystallized from pentane to give 0.061 g (6%) of microfine black needles which were identified as 3-acetyl-2-hydroxypropylidynetricobalt nonacarbonyl, $CH_3C(O)CH_2CH(OH)CCo_3(CO)_9$, m.p. 109 — 111°C (dec.). (Found: C, 31.94; H, 1.48. $C_{14}H_7O_{11}Co_3$ calcd.: C, 31.85; H, 1.34%). IR ($CHCl_3$): terminal CO region, 2105vs, 2013vs, 1977(sh); ν(C=O) 1709 cm^{-1}. NMR ($CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.88—3.17 (m, 2H, CH_2), 4.01 (d, J = 3 Hz, 1H, OH) and 5.18—5.70 (m, 1H, methyne).

(b) 2-Methylallylidynetricobalt nonacarbonyl. A flame-dried three-necked flask, equipped with magnetic stir bar, pressure equalizing dropping funnel and

a nitrogen inlet and outlet was charged with 0.97 g (2.0 mmol) of 2-methylallylidynetricobalt nonacarbonyl in 60 ml of reagent dichloromethane, saturated with carbon monoxide by bubbling the gas just below the surface of the liquid for 15 min and cooled in an ice/water bath. The dropping funnel was charged with 1.28 g (9.6 mmol) of anhydrous aluminum chloride, 0.80 g (10.0 mmol) of acetyl chloride and 40 ml of reagent dichloromethane and stirred to effect solution. The acetyl chloride solution was added dropwise to the cooled mixture over 30 min. The mixture was allowed to come to room temperature and stirred for an additional 2 h. The mixture was poured carefully into water, the layers were separated, and the organic layer was washed once with water and dried over magnesium sulfate. After removal of the solvents under reduced pressure, the products were separated by column chromatography (silicic acid/hexane-dichloromethane 70/30% (v/v)). The first band to be eluted was sublimed in vacuo at 50° C to give 0.20 g (21% by weight) of a mixture of 2-methylallylidynetricobalt nonacarbonyl and 2-methylpropylidynetricobalt nonacarbonyl by comparison of their IR spectra. The second compound to be eluted was recrystallized from pentane to give 0.11 g (10%) of black needles identified as 2-methyl-3-acetylpropylidynetricobalt nonacarbonyl, $(OC)_9Co_3CCH(CH_3)CH_2C(O)CH_3$, m.p. 91—92°C. (Found: C, 34.23; H, 1.85. $C_{15}H_9O_{10}Co_3$ calcd.: C, 34.25; H, 1.73%). IR (CCl_4, cm^{-1}): terminal CO region, 2100s, 2049vs, 2037vs, 2012vs, 1949m; $\nu(C{=}O)$ 1721. NMR (CCl_4): δ 1.50 (d, $J = 15$ Hz, 3H, CH_3), 2.17 (s, 3H, $C(O)CH_3$), 2.77 (d, $J = 15$ Hz, 2H, CH_2) and 4.07 ppm (m, 1H, CH).

Methoxymercuration of allylidynetricobalt nonacarbonyl

To a nitrogen flushed three-necked flask, equipped with pressure equalizing dropping funnel and nitrogen inlet, charged with 1.00 g (2.14 mmol) of allylidynetricobalt nonacarbonyl in 8 ml of absolute methanol, was added dropwise over 15 min a solution of 1.00 g (2.35 mmol) of mercuric trifluoroacetate in 8 ml of absolute methanol. After the mixture had been stirred for 2 h an additional 1.00 g (2.14 mmol) of mercuric trifluoroacetate was added as a solid, and the mixture was stirred for 15 min, then poured into a stirred solution of 1.5 g of NaCl and 1.5 g of $NaHCO_3$ in 50 ml of water. After stirring for 20 min the mixture was filtered on a Buechner funnel. The solid residue was dissolved in 50 ml of chloroform (using a small amount of acetone to help solution), washed with water and dried over $MgSO_4$. The solvents were removed under reduced pressure, and the resulting solid was recrystallized from a chloroform/hexane mixture to give 0.86 g (55%) of black platelets identified as 2-methoxy-3-chloromercuripropylidynetricobalt nonacarbonyl, $(OC)_9Co_3CCH(OCH_3)CH_2HgCl$, m.p. 109—111°C (dec.). (Found: C, 21.13; H, 1.02. $C_{13}H_6O_{10}ClCo_3Hg$ calcd.: C, 21.22; H, 0.82%). IR ($CHCl_3$, cm^{-1}, terminal CO region): 2105s, 2030vs, NMR ($CDCl_3$): δ 2.00—3.00 (m, *ABX*, 2H, CH_2), 3.63 (s, 3H, CH_3) and 4.92—5.13 ppm (m, *ABX*, 1H, CH).

Acknowledgements

The authors are grateful to the National Science Foundation (Grants GP 31429X and MPS75-21215) for generous support of this work and to Dr. Y.M. Cheng for initial experiments on the oxymercuration of $CH_2{=}CHCCo_3(CO)_9$.

References

1 D. Seyferth, G.H. Williams and C.L. Nivert, Inorg. Chem., 16 (1977) in press.

2 D. Seyferth, C.S. Eschbach, G.H. Williams, P.L.K. Hung and Y.M. Cheng, J. Organometal. Chem., 78 (1974) C13.

3 D. Seyferth, Advan. Organometal. Chem., 14 (1976) 97.

4 D. Seyferth, G.H. Williams and J.E. Hallgren, J. Amer. Chem. Soc., 95 (1973) 266.

5 D. Seyferth, G.H. Williams and D.D. Traficante, J. Amer. Chem. Soc., 96 (1974) 604.

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

7 (a) W.T. Dent, L.A. Duncanson, R.G. Guy, H.W.B. Reed and B.L. Shaw, Proc. Chem. Soc., (1961) 169; (b) G. Bor, L. Markó and B. Markó, Chem. Ber., 95 (1962) 333; (c) R. Ercoli, E. Santambrogio and G. Tettamanti-Casagrande, Chim. Ind. (Milano), 44 (1962) 1344.

8 D. Seyferth, J.E. Hallgren and P.L.K. Hung, J. Organometal. Chem., 50 (1973) 265.

9 G.H. Williams, Ph.D. Thesis, Massachusetts Institute of Technology, 1973.

10 P.L.K. Hung, M.Sc. Thesis, Massachusetts Institute of Technology, 1973.

11 C.S. Eschbach, Ph.D. Thesis, Massachusetts Institute of Technology, 1975.

12 (a) I. Wender, S. Metlin, S. Ergun, H.W. Sternberg and H. Greenfield, J. Amer. Chem. Soc., 78 (1956) 5401; (b) I. Wender, H.W. Sternberg and M. Orchin, J. Amer. Chem. Soc., 75 (1953) 3041; (c) G. Karapinka and M. Orchin, J. Org. Chem., 26 (1961) 4187; (d) L. Roos amd M. Orchin, J. Amer. Chem. Soc., 87 (1965) 5502.

13 (a) B.R. James, "Homogeneous Hydrogenation", John Wiley & Sons, New York, 1973, pp. 154—173; (b) J. Kwiatek, in G.N. Schrauzer (Ed.), Transition Metals in Homogeneous Catalysis, Marcel Dekker, Inc., New York, 1971, pp. 25—30.

14 G. Albanese and G. Gavezzotti, Chim. Ind. (Milano), 47 (1965) 1322.

15 D.A. Young, Inorg. Chem., 12 (1973) 482.

16 C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960, pp. 140—143.

17 D. Seyferth, G.H. Williams, A.T. Wehman and M.O. Nestle, J. Amer. Chem. Soc., 97 (1975) 2107.

18 D. Seyferth, M.O. Nestle and A.T. Wehman, J. Amer. Chem. Soc., 97 (1975) 7417.

19 R.N. Haszeldine, J. Chem. Soc., (1953) 3372.

20 S.M. McElvain and C.L. Stevens, J. Amer. Chem. Soc., 69 (1947) 2667.

21 D. Seyferth and M. Takamizawa, J. Org. Chem., 28 (1963) 1142.

22 E. Kiehlmann, P.W. Loo, B.C. Menon and N. McGillivray, Can. J. Chem., 49 (1971) 2964.

23 J. Grignon and M. Pereyre, J. Organometal. Chem., 61 (1973) C33.

24 G. Pályi, F. Piacenti, M. Bianchi and E. Benedetti, Acta Chim. (Budapest), 66 (1970) 127.

25 H. Sternberg, I. Wender and M. Orchin, Inorg. Syn., 5 (1957) 192.