

Preliminary communication

Organocobalt cluster complexes

IX^{*}. A new general route to alkylidynetricobalt nonacarbonyl complexes

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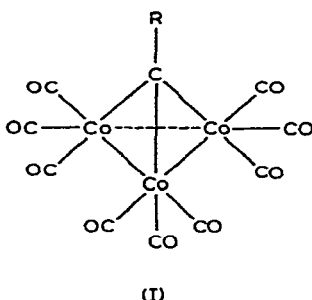
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SUMMARY

Alkylidynetricobalt nonacarbonyl complexes, $RCH_2CCO_3(CO)_9$, where R is alkyl or aryl, were prepared in high yield by the reduction of the appropriate ketones, $RC(O)CCO_3(CO)_9$, with triethylsilane/trifluoroacetic acid in refluxing tetrahydrofuran.

RESULTS AND DISCUSSION

Several routes are available for the preparation of alkylidynetricobalt nonacarbonyl complexes, (I), where R is alkyl¹. Indeed, the first derivative of the $CCO_3(CO)_9$,

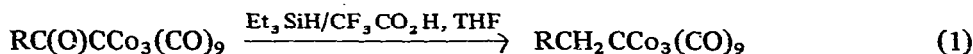


cluster to be reported was the methyl compound, $CH_3CCO_3(CO)_9$, prepared by the acid-induced conversion of acetylenedicobalt hexacarbonyl, $(HC_2H)Co_2(CO)_6$ ². This reaction is capable of generalization but depends on the availability of the required acetylenes.

^{*}Part VIII see ref. 6.

Another potentially general procedure, the reaction of RCX_3 compounds with $Co_2(CO)_8$ or $Co(CO)_4^-$ ion³, suffers from the fact that the organic trihalides required often are not easily available. The reaction of diorganomercury compounds with $HCCO_3(CO)_9$, which gives (I) ($R = aryl$) in excellent yields, proceeds only very slowly and in poor yield with dialkylmercurials⁴. Pályi *et al.*⁵ have reported that halogenated alcohols of type CX_3CR_2OH ($R = H$ or CH_3) react with $Co_2(CO)_8$ to give $R_2CHCCO_3(CO)_9$, rather than the expected $R_2C(OH)CCO_3(CO)_9$ derivatives and have recommended this reaction as a preparative method for the alkyl derivatives. However, the yields obtained were quite low (3–9%), and the exploration of new routes to alkylidynetricobalt nonacarbonyl complexes still merited further consideration. We report here a quite general, high yield preparation of such complexes that is based on readily available starting materials.

Ketones of type $RC(O)CCO_3(CO)_9$ now are relatively easily available, either through reactions of trichloromethyl ketones, $RC(O)CCl_3$, with dicobalt octacarbonyl⁶, or by reaction of mild alkylating agents, such as $RZnX$ or R_4Sn , with our new acylium salts, $[(OC)_9Co_3CCO^+][PF_6^-]$ ⁷ or $(OC)_9Co_3\overset{+}{C}CO\cdots Cl-\bar{Al}Cl_3$ ⁸. We have found that such ketones may be reduced in high, and often nearly quantitative, yield using triethylsilane and trifluoroacetic acid in THF medium [eqn. (1)]. In a typical reduction, a mixture of



3 mmol of the acylmethylidynetricobalt nonacarbonyl, 7 mmol of triethylsilane and 6 mmol of trifluoroacetic acid in 50 ml of dry THF was stirred and heated at reflux under nitrogen for 5 h. The reaction mixture then was cooled and treated with an equal volume of 10% HCl. The organic layer was dried, filtered through a bed of silicic acid and evaporated at reduced pressure. The residue was recrystallized from hexane to give the alkylidynetricobalt nonacarbonyl complex. Our results are summarized in Table 1. It will be noted that

TABLE 1

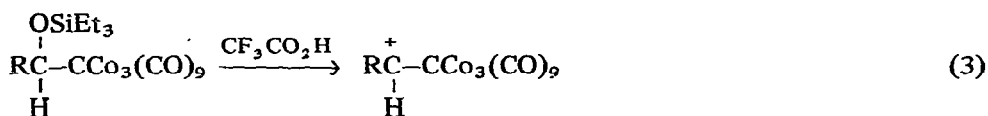
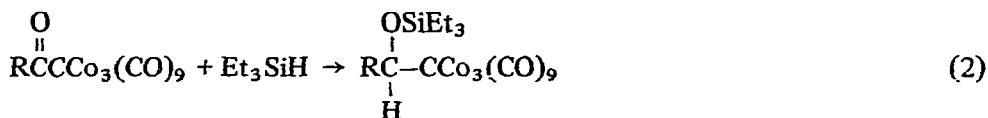
$RCH_2CCO_3(CO)_9$ COMPLEXES BY REDUCTION OF $RC(O)CCO_3(CO)_9$, WITH Et_3SiH/CF_3CO_2H IN THF

R in $RC(O)CCO_3(CO)_9$	$RCH_2CCO_3(CO)_9$ produced (% yield) ^a	M.p. (°C)
CH_3	$CH_3CH_2CCO_3(CO)_9$ (90)	190–192 ^b
C_2H_5	$n-C_3H_7CCO_3(CO)_9$ (92)	121–123 ^b
$n-C_3H_7$	$n-C_4H_9CCO_3(CO)_9$ (87)	58–59
$n-C_4H_9$	$n-C_5H_{11}CCO_3(CO)_9$ (80)	74–75 ^b
$n-C_6H_{13}$	$n-C_7H_{15}CCO_3(CO)_9$ (80)	oil
$(CH_3)_2CH$	$(CH_3)_2CHCH_2CCO_3(CO)_9$ (81)	112–113
cyclo- C_6H_{11}	cyclo- $C_6H_{11}CH_2CCO_3(CO)_9$ (75)	40
C_6H_5	$C_6H_5CH_2CCO_3(CO)_9$ (82)	66–67 ^b
$p-CH_3C_6H_4$	$p-CH_3C_6H_4CH_2CCO_3(CO)_9$ (78)	86–87
$p-BrC_6H_4$	$p-BrC_6H_4CH_2CCO_3(CO)_9$ (67)	94–95

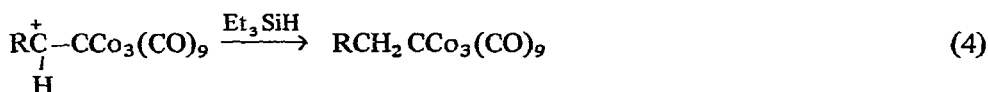
^a All complexes are dark purple in color. Their IR and NMR spectra were in accord with the structures indicated. Satisfactory carbon and hydrogen analyses were obtained for new compounds. ^b Known compound; melting point, IR and or NMR spectrum agreed with that given in the literature.

the examples given are restricted to R primary and secondary alkyl and aryl groups. In the one example of a tertiary alkyl group examined, $(\text{CH}_3)_3\text{CC}(\text{O})\text{CCO}_3(\text{CO})_9$, attempted reduction with $\text{Et}_3\text{SiH}/\text{CF}_3\text{CO}_2\text{H}$ was not successful.

A probable course of this reduction of acylmethyldynetricobalt nonacarbonyls directly to the respective alkyl derivatives is presented in eqn. (2)–(4)*. The facility with which this reduction can be accomplished suggests that carbonium ions of type (II) are



(II)



readily accessible, and further studies in these laboratories¹¹ have confirmed this idea.

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*The acid-catalyzed addition of organosilicon hydrides to carbonyl compounds has been studied in detail by Calas and his coworkers⁹, the reduction of carbonium ions using the $\text{Et}_3\text{SiH}/\text{CF}_3\text{CO}_2\text{H}$ system by Carey *et al.*¹⁰.

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