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A NOVEL ONE-STEP SYNTHESIS OF ALKYLIDYNE TRICOBALT NONACARBONYL CLUSTER COMPLEXES FROM DITHIOESTERS.

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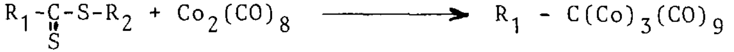
Dithioesters react with dicobalt octacarbonyl in ethanol to afford in one step good yields of various alkylidyne tricobalt nonacarbonyl clusters.

Several procedures for the preparation of alkylidyne tricobalt nonacarbonyl clusters have been developed and reviewed recently (1)(2). Among them only two routes allow direct synthesis of the clusters by reaction of dicobalt octacarbonyl either with terminal acetylenes or with polyhalides. The first one is not always successful and is limited to the synthesis of complexes with a methylene attached to the apical carbon atom. The second one although more general needs the preliminary synthesis of R-CX_3 derivatives which does not allow access to clusters substituted by a branched aliphatic chain. Other routes are indirect and based on the reaction of preformed H-$C(Co)_3(CO)_9$ with organomercurials (3) or Br-$C(Co)_3(CO)_9$ with Grignard reagents (4) or with arenes in a Friedel-Crafts type reaction (5).

In this paper we want to describe a novel one-step synthesis of alkylidyne tricobalt nonacarbonyl cluster complexes which overcome several of the limitations notified before.

We have previously described the reaction of O-Alkyl S-Alkyl dithiocarbonates (or S-Alkyl xanthates) with $Co_2(CO)_8$ which lead to alkoxy-alkylidyne tricobalt nonacarbonyl clusters (6). So it seemed reasonable to think that dithioesters, which are readily prepared (7), would react similarly to afford the titled clusters.



$$R_1-\underset{\overset{\|}{S}}{C}-S-R_2 + Co_2(CO)_8 \longrightarrow R_1 - C(Co)_3(CO)_9$$

In a typical experiment $Co_2(CO)_8$ (7,5 millimoles) was dissolved in absolute ethanol (40 ml) and left at room temperature under nitrogen for one hour. Addition of the dithioester (5 millimoles) was followed by warming at 70°C for two hours. After concentration of the solution the cluster was purified by TLC on silica plates (elution with hexane) and the black or deep-red crystals were crystallized from pentane. The clusters obtained by this way are listed in the table.

Table : R in R-C$(Co)_3(CO)_9$

R	mp(°C) (litt.)	% yield (litt.)	R	mp(°C) (litt.)	% yield (litt.)
CH_3-	183-185 (9)	44 43 (9)	pMe-C_6H_4-	105-106 (3)	53 31 (3)[a]
C_2H_5-	190-192 (8)	47 36 (8)[a]	pMeO-C_6H_4-	95-98 (3)	74 22 (3)[a]
$\genfrac{}{}{0pt}{}{CH_3\diagdown}{CH_3\diagup}CH-$	158-160 (decomp)	35	diMe-3,4-C_6H_3-	127-129	49
			p$(CH_3)_2N$-C_6H_4-	125-126 -	51 10 (4)[a]
CH_3-$(CH_2)_3$-	74-75 (8)	42 43 (8)[a]	2-thiophenyl	116-118	65
Cyclohexyl	90-92	33	α-naphthyl	88-90 (3)	45 13 (4)[a]
C_6H_5-	105-107 (9)	68 32 (3)[a]			

a. calculated yields based on the yield of the preformed clusters.

The structure is supported by NMR data and IR spectra (absorptions at 2100-2000 cm^{-1} from non-bridging carbonyls). The new compounds have been characterized by their elemental analysis and mass spectra.

Our results show that this new route is very convenient for direct synthesis of various alkylidyne tricobalt nonacarbonyl clusters including compounds which have not been prepared by other ways (R = isopropyl, cyclohexyl). In some cases a small amount of the cluster CH_3-S-C-$(Co)_3(CO)_9$ already mentioned (6) has been isolated which suggest that desulfurization occurs via elimination steps, the S-CH_3 grouping being much more easily removed than the R groups (carbon-carbon bond). Although no evidence has been found we think that desulfurization can occur via successive radical pathways as proposed for the reaction of polyhalides with cobalt carbonyl (10).

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