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Preliminary communication

Organocobalt cluster complexes
X*. Evidence for the methylidynetricobalt nonacarbonyl radical

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SUMMARY

The azobisisobutyronitrile-initiated addition of $HCCo_3(CO)_9$ to the C=C bonds of allyl acetate and allyl ethyl ether to give $(OC)_9Co_3C(CH_2)_3O_2CCH_3$ and $(OC)_9Co_3C(CH_2)_3OC_2H_5$, respectively, demonstrated the accessibility of the $\cdot CCo_3(CO)_9$ radical.

The arylation and alkylation of the carbon atom of the $CCo_3(CO)_9$ cluster by reaction of a diorganomercury compound with methylidynetricobalt nonacarbonyl is a useful reaction[2]. No direct evidence concerning the mechanism of this process is available, but we believe, on the basis of rather indirect evidence, that a radical mechanism obtains. If this is so, then the $\cdot CCo_3(CO)_9$ radical should be accessible by other means. We find that this is the case.

Among the radical reactions of the carbon–hydrogen bond is its radical-initiated addition to the C=C bond of olefinic compounds, *e.g.*, the addition of chloroform to olefins, $RCH{=}CH_2$, to give $CCl_3CH_2CH_2R$, via a radical chain process[3]. The C–H bond of methylidynetricobalt nonacarbonyl adds to olefins in this manner.

A 100 ml, three-necked flask equipped with a magnetic stirring assembly, a reflux condenser topped with a gas outlet tube, and a gas inlet tube was charged with 3.0 mmol of $HCCo_3(CO)_9$, 30 ml of allyl acetate and 0.007 g (0.006 mmol) of azobisisobutyronitrile (AIBN)**. Carbon monoxide was bubbled slowly through the solution at room temperature for 30 min and then the mixture was heated to 80° while the carbon monoxide

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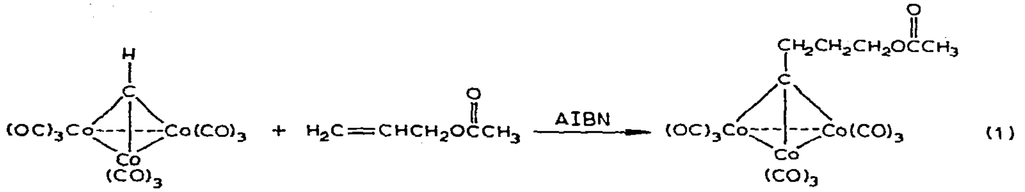
* For part IX see Ref. 1.
** No reaction occurred in the absence of this catalyst.

stream was continued. After 24 h, an additional 7 mg of AIBN was added and the heating was continued. Further 7 mg quantities of AIBN were added until a total of 18 mole % had been added over the course of 9 days. The reaction mixture was filtered, the filtrate was evaporated and the residue was taken up in dichloromethane and purified using column chromatography (100 mesh silicic acid, CH_2Cl_2 eluant). Obtained were 0.60 g (46%) of starting $HCCo_3(CO)_9$, m.p. 104–106° (dec), and a red crystalline solid which was recrystallized from hexane to give 0.35 g (21%) of 4-acetoxybutylidynetricobalt nonacarbonyl, m.p. 108–109° (eqn.1). (Found: C, 33.63; H, 1.82. $C_{15}H_9O_{11}Co_3$ calcd.: C, 33.24; H, 1.67%). The IR spectrum (in CCl_4) showed the ester C=O band at 1740 cm^{-1} and the ligand C≡O frequencies at 2090, 2050, 2030, 2010 and 1965 cm^{-1}. NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3CO), 3.03 (quintet, 2H, $CH_2\underline{CH_2}CH_2$) and 4.0–4.6 ppm (4H, methylene).



(1)

A similar reaction of $HCCo_3(CO)_9$ with allyl ethyl ether, carried out at 80° under carbon monoxide for 8 days, with incremental addition of a total of 20 mole % of AIBN, gave a 41% recovery of starting cobalt cluster and 4-ethoxybutylidynetricobalt nonacarbonyl, a red solid with m.p. 54–56°, $(OC)_9Co_3C(CH_2)_3OEt$, in 18% yield. (Found: C, 34.05; H, 2.03. $C_{15}H_{11}O_{10}Co_3$ calcd.: C, 34.11; H, 2.01%.) IR (in CCl_4; CO region): 2115, 2060, 2040, 2020, 1975 cm^{-1}. NMR ($CDCl_3$): δ 1.20 (t, 3H, CH_3), 2.13 (quintet, 2H, center CH_2) and 3.33–3.91 (three overlapping triplets, 6H).

Although the product yields are low and the reaction times are long, these reactions establish the accessibility of the methylidynetricobalt nonacarbonyl radical. Other reactions of this radical and other routes which serve in its generation are under investigation.

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