Tetrahedron Letters No.25, pp. 2217-2220, 1970. Pergamon Press. Printed in Great Britain.

NOVEL CARBONYLATION REACTION OF SUBSTITUTED METHINYL TRIS(TRICARBONYLCOBALT) COMPLEXES

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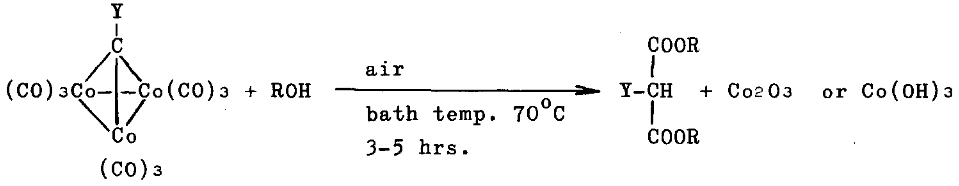
(Received in Japan 18 March 1970; received in UK for publication 29 April 1970)

Recently great interest has centered around transition metal cluster complexes. Substituted methinyl tris(tricarbonylcobalt) complexes, $YC\text{-}Co_3(CO)_9$ (1~6) (where Y represents hydrogen, alkyl, aryl, halogen, -COOH, -COOR, $-CH_2CH_2COOH$, -CH=CHCOOH, etc.), have been known to possess the structure containing an aliphatic carbon atom triply bridged to three metal atoms.(7) However, their chemical reactivity and catalytic action have little been investigated. We wish to report a novel carbonylation reaction of substituted methinyl tris(tricarbonylcobalt) complexes.

Ethylidyne tris(tricarbonylcobalt) ($I:Y=CH_3$) was prepared by strong acid treatment of the acetylene complex, obtained from octacarbonyl dicobalt and acetylene. A methanolic solution of (I) was heated gently at about 70°C with bubbling of air. The reaction mixture was cooled and the resulting cobalt oxide (or cobalt hydroxide) was removed by filtration. An oily product was isolated by preparative g.l.c., and identified as dimethyl methylmalonate (80% yield) by nmr and mass spectra. No other product was detected.

This reaction represents the first example of dicarbonylation reactions on the same carbon atom with metal carbonyl. A similar treatment of the methinyl derivative (II:Y=H) in alcohol resulted in the formation of malonates (40% yield).



I : $Y = CH_3$ $R = CH_3$

II : $Y = H$ $R = C_2H_5$

This novel carbonylation of (I) occurred also by addition of organic bases (pyridine or tertiary organophosphines) under CO pressure. For example, in the presence of tri-n-butylphosphine, methanolysis of (I) yielded 14% methyl propionate, 61% dimethyl methylmalonate and 5% dimethyl succinate. As shown in the table, the composition of the products may vary with CO pressure and the basicity of the additives.

TABLE

Carbonylation Reaction of $CH_3C\text{-}Co_3(CO)_9$ (I) in the Presence of Organic Base under CO pressure (solvent, methanol; concentration of (I), 22 mmoles/l; base/cobalt = 1/1; reaction temperature 160°C)

Base	CO pressure (atm)	Yield (%)		
		Methyl propionate	Dimethyl methylmalonate	Dimethyl succinate
Pyridine	20	50	9	7
Pyridine	50	69	4	9
Pyridine	100	52	8	21
Pyridine	150	53	12	20
PPh_3	100	28	38	11
PBu_3	100	14	61	5
PEt_3	100	19	43	3

In the presence of pyridine, the yield of dicarbonylation products is dependent on CO pressure. On the other hand, on addition of tertiary organophosphine, the yield is independent of CO pressure, but dependent on the basicity of the added tertiary organophosphine. The cobalt carbonyl compounds isolated from the reaction mixtures were identical in properties and infrared spectra with authentic bis [(tertiary organophosphine) tricarbonylcobalt], $[Co(CO)_3(PR_3)]_2$. Dimethyl succinate, an isomer of dimethyl methylmalonate, may be formed from the carbonylation of acrylate. Indeed the existence of acrylate was observed by g.l.c. in the course of this reaction process.

Furthermore, when sodium methoxide was used in methanol solution, methylmalonate was obtained in 50% yield under nitrogen.

The organic products obtained from methanolysis of (I) under hydrogen pressure were identified as methyl propionate and 1,1-dimethoxypropane. In this system, the ratio of the former to the latter depends on the concentration of (I). Under the same pressure of hydrogen, the increase in the concentration of (I) has led to the decrease of the formation of the methanol cleavage product. For example, under the conditions (reaction temperature 120°C; hydrogen pressure 100 atm) at the concentration of 15 mmoles/l of (I), the carbonylation product consisted of 36% methyl propionate and 64% 1,1-dimethoxypropane, whereas in the case of 22 mmoles/l, the ratio was 16/84.

In benzen solution, hydrogenolysis of (I) gave propionaldehyde in 15% yield. In the presence of hydrogen and carbon monoxide, however, the yield of propionaldehyde increased to 50%.

This investigation is in progress, and details will be reported in near future.

References

1. U. Kruerke and W. Hubel, Chem. & Ind. (London), 1264 (1960)
2. W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, Proc. Chem. Soc., 169 (1961)
3. G. Bor, L. Marko and B. Marko, Chem. Ber., **95**, 333 (1962)
4. R. Erocoli, E. Santambrogio, C. T. Casagrande, Chem. Ind. (Milan), **44**, 1344 (1962)
5. G. Albanesi and E. Gavezotti, Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis. Mat. Nat., **41**, 497 (1966)
6. B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, Chem. Comm., 529 (1967); J. Chem. Soc. A, 691 (1969)
7. P. W. Sutton and L. G. Dahl, J. Amer. Chem. Soc., **89**, 261 (1967)