Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Novel nucleophilic properties of the decacarbonyltricobaltate mono-anion

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(Received May 27th, 1970; in revised form August 3rd, 1970)

We recently reported the preparation of the decacarbonyltricobaltate mono-anion, $[Co_3(CO)_{10}]^-$ (I) via reduction of octacarbonyldicobalt by alkali metals in diethyl ether[1]. The infrared spectrum of this ion, both in solution and in the solid state, exhibited an absorption in the vicinity of 1600 cm^{-1} which we associated with a triply bridging carbonyl group. The rather low frequency[2-4] of this absorption suggested the possibility that the carbon—oxygen bond order was lowered with localization of the negative charge on the oxygen atom. This shift toward alkoxide character, in turn, suggested the possibility of preparing enneacarbonyltricobaltmethoxy derivatives by nucleophilic reaction of this anion with appropriate halides.

Accordingly, when a toluene solution of trimethylamineiodoborane[5] was added to the solid sodium salt of (I), the known trimethylamine(enneacarbonyltricobaltmethoxy)-borane[3] (II) was isolated (71% yield) after recrystallization from hexane.

$$\underset{\text{(I)}}{Na[Co_3(CO)_{10}]} + Me_3NBH_2I \rightarrow \underset{\text{(II)}}{Me_3NBH_2{-}OCCo_3(CO)_9} + NaI$$

This derivative was identified by elemental analysis and by comparison of its infrared spectrum with that of an authentic sample prepared according to the procedure of Klanberg *et al.*[6].

Similarly, the lithium salt of (I) was found to react with trimethylchlorosilane and triphenylchlorosilane in diethyl ether to yield the corresponding red-black siloxy derivatives (IIIa) and (IIIb) shown in Fig.1.

$$R_3SiCl + \underset{\text{(I)}}{Li[Co_3(CO)_{10}]} \rightarrow \underset{\text{(IIIa,b)}}{R_3Si{-}OCCo_3(CO)_9} + LiCl$$

(a, R = Me; b, R = Ph)

The trimethylsiloxy derivative (IIIa), obtained in 44% yield after recrystallization from hexane, sublimed at 80° in a sealed evacuated tube, the unsublimed material melting with decomposition at 108° (uncorr.). The triphenylsiloxy derivative (IIIb), (m.p. 91–93° uncorr., 20% yield) was also recrystallized from hexane. All preparative work was done

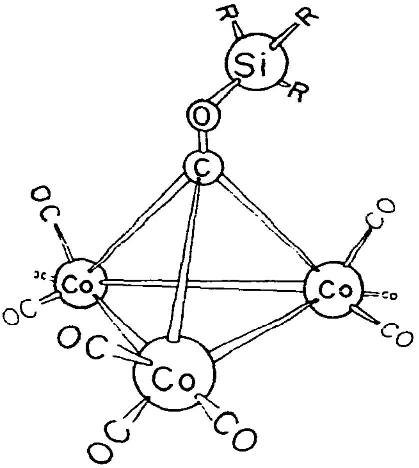

Fig.1. (III a, b)

under an atmosphere of dry nitrogen. These derivatives gave satisfactory elemental analyses and infrared spectra similar to that of (II) and of reported methinylenneacarbonyltricobalt derivatives[7]. Thus, the infrared spectrum of (IIIa) in hexane showed peaks at 2105w, 2051 vs, 2034s and 2015w cm^{-1}. The infrared spectrum of (IIIb) in the carbonyl stretching region was identical to that above within experimental error. The mass spectrum of (IIIa) was recorded and exhibited a parent peak at $m/e = 530$.

Although there are several examples of Lewis base activity by the carbonyl group of coordinated carbon monoxide[8,9], the work presented here describes the first actual nucleophilic displacement reaction by this ligand.

ACKNOWLEDGEMENTS

We thank the National Research Council of Canada for financial support and for scholarships to A.J.C. and B.H.F.; C.D.M.M., S.A.F. and B.H.F. also thank the Government of the Province of Ontario for the award of Province of Ontario Graduate Fellowships. S.A.F. also thanks the University of Manchester Institute of Science and Technology for the award of the Lionel Blundell Overseas Fellowship.

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