

Preliminary communication

FORMATION OF $\text{Fe}_3(\text{N}\equiv\text{CMe})(\text{CO})_9$, DURING THE REACTION OF $\text{Fe}_3(\mu_3\text{-CMe})(\text{CO})_{10}\text{X}$ CLUSTERS WITH ALKYNES ($\text{X} = \text{NO}$) OR DIAZOALKANES ($\text{X} = \text{H}$). FIRST EXAMPLES OF ETHYLIDYNE-NITROGEN COUPLING TO ACETONITRILE

DIDIER NUEL and RENÉ MATHIEU*

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'UPS, 205 route de Narbonne, 31400 Toulouse (France)

(Received February 25th, 1986)

Summary

Reaction of the clusters $\text{Fe}_3(\mu_3\text{-CCH}_3)(\text{CO})_{10}\text{X}$ with alkynes ($\text{X} = \text{NO}$) or diazoalkanes ($\text{X} = \text{H}$) lead among other products to the cluster $\text{Fe}_3(\text{CH}_3\text{CN})(\text{CO})_9$ in yields varying from 1 to 18%, the acetonitrile ligand resulting from the coupling of the ethylidyne ligand with nitrogen.

During the course of our studies on the reactivity of alkylidyne ligands bonded to trinuclear clusters of iron [1–4], we were interested in the study of the reactivity of the cluster $\text{Fe}_3(\mu_3\text{-CCH}_3)(\text{CO})_{10}\text{NO}$ (1) [5], toward alkynes and of the reactivity of the cluster $\text{HFe}_3(\mu\text{-CCH}_3)(\text{CO})_{10}$ (2) [6], toward diazoalkanes. In both cases a small amount of the unexpected complex 3 was formed.

Reaction of 1 with $\text{RC}\equiv\text{CR}$ alkynes ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) in boiling hexane gave ferrole complexes $\text{Fe}_2(\text{CO})_6(\text{RCCR})_2$ [7] as the main products and trace quantities (1% yield) of a brown complex 3 with spectroscopic properties in exact agreement with published data [8] for the complex $\text{Fe}_3(\text{N}\equiv\text{CCH}_3)(\text{CO})_9$ (IR $\nu(\text{CO})$ (hexadecane): 2087m, 2037s, 2027s, 2015s, 1995m, 1983m, 1976w cm^{-1} ; $\nu(\text{CN})$ (KBr): 1615 cm^{-1} ; ^1H NMR (CDCl_3) 3.44 ppm; mass spectrum $m/e = 461$ and successive loss of 9CO. Literature data [8]: IR $\nu(\text{CO})$ (hexane): 2086m, 2037s, 2027s, 2015s, 1993m, 1983m, 1975w cm^{-1} ; $\nu(\text{CN})$ (C_2Cl_4): 1610 cm^{-1} ; ^1H NMR (CDCl_3): 3.43 ppm). The presence of alkyne is necessary for the formation of 3, heating of 1 alone or in the presence of PPh_3 giving no trace of it.

In the case of complex 2, reaction with N_2CPh_2 or $\text{N}_2\text{CHC}(\text{O})\text{OEt}$ for a few minutes in boiling toluene gave 3 in 1 and 2% isolated yield, respectively, along with other products which have not yet been fully identified. In the case of

N_2CPh_2 , the reaction is carried out at room temperature and **3** is the only product detected by infrared spectroscopy. It is isolated in 18% yield after purification by chromatography. The mechanism of these two reactions is not clear (the role of the alkyne in the reaction with **1**, and the mode of decomposition of the N_2CR_2 molecule in the reaction with **2** are uncertain) and is presently under investigation*. Nevertheless, the two reactions indicate that coupling of the ethylidyne ligand with nitrogen is quite an easy reaction, and the nitrogen source can be either a nitrosyl ligand or the diazoalkane molecule.

These represent, to our knowledge, the first cases of coupling of a carbyne ligand to nitrogen to give a nitrile ligand, though the reverse reaction has been observed in the interaction of $\text{W}_2(\text{OBU}^t)_6$ with nitriles [9].

References

- 1 D. de Montauzon and R. Mathieu, *J. Organomet. Chem.*, **252** (1983) C83.
- 2 F. Dahan and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, (1984) 432.
- 3 D. Nuel, F. Dahan, and R. Mathieu, *J. Am. Chem. Soc.*, **107** (1985) 1658.
- 4 D. Nuel, F. Dahan, and R. Mathieu, *Organometallics*, **4** (1985) 1436.
- 5 D. Nuel and R. Mathieu, unpublished results.
- 6 M. Lourdichi, Thèse de 3ème Cycle, Toulouse, 1983; W.K. Wong, K.W. Chim, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett, and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1983) 1557.
- 7 W.P. Fehlamer and H. Stolzenberg, in G. Wilkinson and F.G.A. Stone, Eds., *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 4, p. 548.
- 8 M.A. Andrews and H.D. Kaesz, *J. Am. Chem. Soc.*, **101** (1979) 7255.
- 9 R.R. Schrock, M.L. Listerman, and L.G. Sturgeooff, *J. Am. Chem. Soc.*, **104** (1982) 4291.

*Note added in proof. After this paper was submitted a preliminary communication appeared (A. Goldhaber, K.P.C. Vollhardt, E.C. Walborsky and M. Wolfgruber, *J. Am. Chem. Soc.*, **108** (1986) 516) giving another example of nitrile synthesis from the reaction of a carbyne ligand and NO with trinuclear cobalt complexes. The first reaction step is insertion of NO into the Co—C bond, deoxygenation being effected by the action of carbon monoxide.