Journal of Organometallic Chemistry, 157 (1978) C19—C20

Preliminary communication

THE CYANATION OF ACETYLACETONE BY CYANOGEN CATALYZED BY [Ni(acac)$_2$]

B. CORAIN

Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione, C.N.R., Istituto di Chimica Analitica, University of Padova, 35100 Padua (Italy)

(Received June 5th, 1978)

Summary

The addition of cyanogen to acetylacetone is catalyzed by [Ni(acac)$_2$] in CH_2CH_2 under ambient conditions. The product is not formed by a simple addition of C_2N_2 to the methino position of Hacac, since 3-cyanoimminoacetylacetone is not formed. Cyanogen reacts stoichiometrically with [Ni(acac)$_2$] to give the novel compound [Ni(acac C_2N_2)$_2$].

In studies of activation of cyanogen by metal complexes [1—4], we have recently focused our attention on the behaviour of this "small" molecule toward metal complexes containing a metal atom in a "normal oxidation" state, as, for example, in acetylacetonate complexes.

The appearance of the paper by Eckberg et al. on [Ni(acac)$_2$]-catalyzed addition of isocyanates and other electrophiles to Hacac [5] prompts us to report preliminary results on cyanogen activation by [Ni(acac)$_2$], and the related catalytic cyanation of acetylacetone.

We find that [Ni(acac)$_2$] reacts rapidly and quantitatively with cyanogen in dichloromethane under ambient conditions to give a brick red microcrystalline product, m.p. 248—250°C, with the stoichiometry [Ni(acac)$_2$·2(C_2N_2)] (Found: C, 45.63; H, 3.79; N, 15.05. Calcd.: C, 46.58; H, 3.89; N, 15.52%) after recrystallization from dichloroethane).

The IR spectrum of this complex displays significant bands at 3180s (ν(=N—N)), 2220(vw) (ν(C≡N)) and 1640s (ν(C=N)) cm^{-1} (KBr disc) together with a pattern of bands in the range 1600—400 cm^{-1} attributable to coordinated substituted-acetylacetonato ligands [6]. These results strongly suggest that cyanogen is not simply coordinated to the metal, but instead has inserted into the methino C—H bond (as was observed for the electrophiles considered in ref. 5) to give two cyanoimminoacetylacetonato ligands (ciacac) coordinated to one nickel atom.

If the reaction is carried out in the presence of an excess of Hacac and

TABLE 1

CATALYTIC ADDITION OF CYANOGEN TO ACETYLACETONE AT CA. 20°C $[Ni(acac)_2]$ 1.20 × 10^{-2} *M*; $[C_2N_2]$ 0.54 *M*; [acac] 0.46 *M*.

Time	% reaction (residual substrate)
1.45	60
4.00	49
22.00	39
48.00	14

C_2N_2, cyanation can be achieved under mild conditions and in higher yields. If a dichloromethane solution ca. 0.5 *M* in both C_2N_2 and Hacac is made ca. 10^{-3} *M* in $[Ni(acac)_2]$ at ca. 20°C, the initially pale green color turns gradually to brown and eventually dark red, as a brown precipitate forms. GLC analysis of the surnatant solution allows the consumption of Hacac to be followed and the results of a typical experiment are summarized in Table 1.

The organic product is a beige powder melting at 205—209°C with elemental analysis very close to the composition $C_7H_8N_2O_2$ Found: C, 54.10; H, 5.35; N, 17.73. Calcd.: C, 55.25; H, 5.29; N, 18.41%.

Cyanation of Hacac by cyanogen catalysed by ethoxide ion is known to give 3-cyanoimminoacetylacetone ($C_7H_8N_2O_2$), a white compound melting at 128—129°C, but the IR and UV spectra of this species are quite different from those of the nickel(II)-catalyzed reaction product.

Work is in progress to clarify the nature of the complex $Ni(ciacac)_2$ and of the product of the relevant catalytic process, as well as the behaviour of other metal acetylacetonates towards cyanogen.

References

1 M. Bressan, G. Favero, B. Corain and A. Turco, Inorg. Nucl. Chem. letters, 7 (1971) 197.
2 G. Favero, B. Corain, P. Rigo and A. Turco, Gazz. Chim. Ital., 103 (1973) 297.
3 B. Corain, M. Basato and G. Favero, J. Chem. Soc. Dalton, (1977) 2081.
4 B. Corain, M. Basato and A. Warsame, Chim. Ind. (Milan), in press.
5 R.P. Eckberg, J.H. Nelson, J.W. Kenney, P.N. Howells and R.A. Henzy, Inorg. Chem., 16 (1977) 3128.
6 (a) J.P. Collman, Angew. Chem. Internat. Edit., 4 (1965) 132; (b) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, J. Wiley, New York, 1963.
7 W. Traube, Chem. Ber., 31 (1898) 191.