Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PREPARATION AND PROPERTIES OF SOME BIS-ORGANONITRILE NICKEL COMPOUNDS

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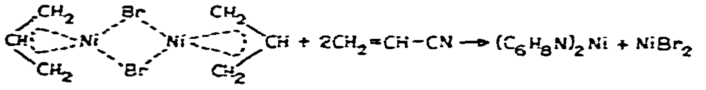
(Received November 29th, 1965)

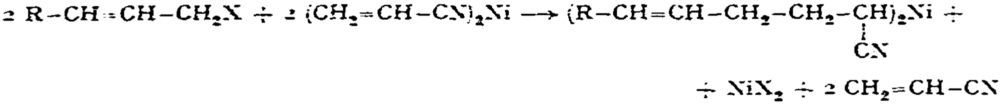
In an earlier paper[1] we reported on the formation of the complex $[CH_2{=}CH{-}CH_2{-}CH_2{-}CH(CN)]_2Ni$ in the reaction of di-π-allylnickel bromide[2] with acrylonitrile. The same compound can be prepared from allyl bromide, nickel carbonyl and acrylonitrile. The reactions involved can be represented as follows:



(1)

$$2CH_2{=}CH{-}CH_2Br + 2CH_2{=}CH{-}CN + 2Ni(CO)_4 \rightarrow (C_6H_8N)_2Ni + NiBr_2 + 8CO \qquad (2)$$

In order to get a general synthetic approach to this class of compounds and to obtain further information concerning their structure, the reaction (2) was extended to $R{-}CH{=}CH{-}CH_2Br$ having $R = CH_3$, C_6H_5. Since it was difficult to isolate complexes prepared from $R{-}CH{=}CH{-}CH_2Cl$ by reaction (2), owing to the easy polymerization of the allylic chloride, we investigated a more versatile reaction. The following, which starts from bisacrylonitrilenickel[3], proved to be effective:



$$2\ R{-}CH{=}CH{-}CH_2X + 2\ (CH_2{=}CH{-}CN)_2Ni \longrightarrow (R{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{C}}H)_2Ni + NiX_2 + 2\ CH_2{=}CH{-}CN \qquad (3)$$

$R = H, CH_3, C_6H_5;\ X = Br, Cl.$

By reaction (3) we prepared the class of compounds with the elementary formula $[R'{-}CH_2{-}CH(CN)]_2Ni$, where R' is $CH_2{=}CH{-}CH_2$, $CH_3{-}CH{=}CH{-}CH_2$, $C_6H_5{-}CH{=}CH{-}CH_2$, $C_6H_5CH_2$, or C_6H_5. Benzyl chloride and iodobenzene react with bisacrylonitrilenickel, but yields are low; alkyl halides do not react. Coupling reactions, leading to products $R{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}R$, can also occur as side reactions.

Similarly to the previously reported[1] bis(1-cyano-4-penten-1-yl)nickel*, all the complexes obtained by reaction (3) are vitreous, dark-orange solids. They are very sensitive to oxygen, and are soluble in benzene, chloroform, carbon disulphide, and slightly soluble in n-hexane. The analyses are in agreement with the expected formulas.

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* Previously named in a shortened, but less correct form, bis(5-hexenenitrile)nickel.

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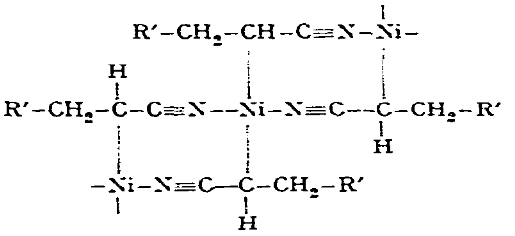
Cryoscopic data in benzene are indicative of a very high molecular weight; we were unable to make osmotic determinations because of the instability of the complexes. All the products are diamagnetic. Their IR spectra show a C≡N stretching band at 2220 cm^{-1}; the bands associated with allylic double bonds or a phenyl group do not appear to be affected by coordination. The NMR spectrum shows poorly resolved, broadened peaks corresponding to the protons adjacent to nickel atom; the other protons give sharper peaks.

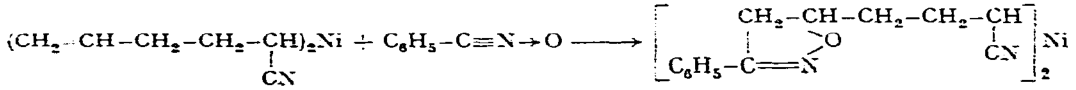
The complexes give rise to the nitriles, R'-CH$_2$-CH$_2$-CN, by reaction in benzene solution with anhydrous hydrochloric acid under nitrogen; the same reaction occurs in methyl alcohol containing a little water, but more slowly. Thermal decomposition of the complexes, *in vacuo* at 140–180°, yields metallic nickel and a mixture of two nitriles, R'-CH=CH-CN and R'-CH$_2$-CH$_2$-CN. The compounds described in the present paper do not react with hydrogen at atmospheric pressure.

STRUCTURE

On the basis of the above data, the following polymeric structure can be postulated:



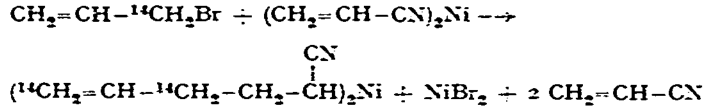
The IR spectroscopical evidence for the absence of coordination of the R' group is confirmed on chemical grounds when the complex [CH$_2$=CH-CH$_2$-CH$_2$-CH(CN)]$_2$Ni is allowed to react with benzonitrile oxide, a typical reagent for olefins[4]. Bis[1-cyano-3-(3-phenylisoxazolin-5-yl)prop-1-yl]nickel is obtained without affecting the coordination to the nickel atom:



That coordination occurs through C≡N group is supported by the diamagnetism and infrared spectra. The C≡N frequency is the same as is in NC-CH$_2$-Co(CO)$_3$-P(C$_6$H$_5$)$_3$[5]: the downward shift (R'-CH$_2$-CH$_2$-C≡N, C≡N = 2238 cm^{-1}) can be explained, as it was recently made for (CH$_2$=CH-CN)$_2$Mo(CO)$_2$[6], by taking into account the ability of C-Ni bond to aid the nitrile group in accepting back charge from the metal. In this way the C≡N group can become coordinated with the metal without increasing its bond order.

MECHANISM OF FORMATION

The mechanism of formation of these complexes was studied by radioisotopically labelled compounds. Reaction (3), carried out with $CH_2{=}CH{-}^{14}CH_2Br$, proceeded as follows:

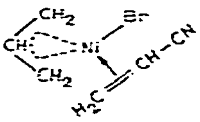


$$CH_2{=}CH{-}^{14}CH_2Br + (CH_2{=}CH{-}CN)_2Ni \longrightarrow$$
$$(^{14}CH_2{=}CH{-}^{14}CH_2{-}CH_2{-}\overset{CN}{\overset{|}{C}H})_2Ni + NiBr_2 + 2\ CH_2{=}CH{-}CN$$

The complete rearrangement ($^{14}C_4 = {}^{14}C_6 = 50\%$) of allylic group in bis(1-cyano-4-penten-1-yl)nickel was established by decomposing the complex with hydrogen chloride and ozonolyzing the 5-hexenenitrile[7] thus formed. On the other hand, the unreacted allyl bromide recovered after completion of reaction was not rearranged. The absence of any reaction of the type:

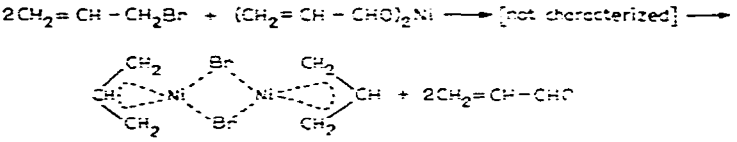
$$CH_2{=}CH{-}^{14}CH_2Br \rightleftarrows {}^{14}CH_2{=}CH{-}CH_2Br$$

suggests that, in a first stage bisacrylonitrilenickel coordinates with allyl bromide. As soon as the halide group is split off, the C_1 and C_3 carbon atoms in the allylic group become equally able to react with coordinated molecules of acrylonitrile:



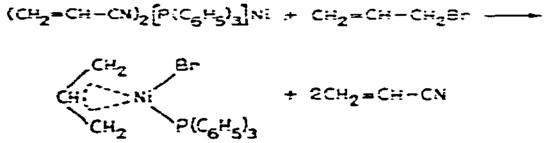
(I)

In a second stage a rearrangement involving a reduction–oxidation process occurs with formation of complexes corresponding to the structure $[R'{-}CH_2{-}CH(CN)]_2$-Ni. The suggestion of the intermediate formation of (I) is supported by the reaction of allyl bromide with bisacroleinnickel[8] which gave rise to a complex which was not well characterized. By heating it carefully *in vacuo*, di-π-allyl nickel bromide sublimed as dark red crystals:



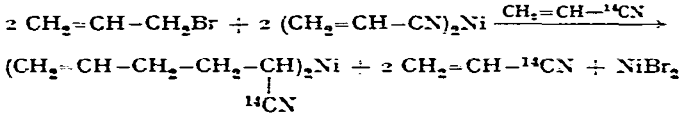
This behaviour indicates that the intermediate complex must have contained both allyl bromide and acrolein.

Furthermore, π-allylbromo(triphenylphosphine)nickel was obtained by the reaction of allyl bromide with bisacrylonitrile(triphenylphosphine)nickel[3]:



The presence of triphenylphosphine ligand prevents acrylonitrile from remaining coordinated as it is in (I).

The compound (I) is also the intermediate in reactions (1) and (2). In the intermediate stage, acrylonitrile can exchange with uncoordinated acrylonitrile. By carrying out reaction (3) in the presence of ^{14}C acrylonitrile, the bis(1-cyano-4-penten-1-yl)nickel obtained was found to be radioactive. Its specific activity was equal to the activity calculated for a reaction in which exchange is complete:



$$2\,CH_2{=}CH{-}CH_2Br + 2\,(CH_2{=}CH{-}CN)_2Ni \xrightarrow{CH_2=CH-{}^{14}CN} (CH_2{=}CH{-}CH_2{-}CH_2{-}\underset{^{14}CN}{\underset{|}{CH}})_2Ni + 2\,CH_2{=}CH{-}{}^{14}CN + NiBr_2$$

Bisacrylonitrilenickel, on the contrary, did not exchange under these conditions. This does not indicate that di-π-allylnickel bromide has been formed, because di-π-allylnickel bromide in this case would have caused the rearrangement of unreacted allyl bromide[9].

This mechanism also explains why reaction (3) occurs only with halides which are able to coordinate with nickel through allylic or aromatic double bonds.

EXPERIMENTAL

Infrared spectra were run by Dr. C. A. CESELLI on a Perkin–Elmer Model 21 instrument, and nuclear magnetic resonance spectra were obtained by Dr. M. TACCHI VENTURI on a 60 megacycles Perkin–Elmer Model R10 NMR spectrometer.

Preparation of the complexes

Since the method of preparation was essentially the same for all complexes, only the general features will be described. All the operations must be carried on under a stream of argon.

A mixture of bisacrylonitrilenickel (2 g, 12 mmoles) and aryl-alkyl halide (15 mmoles) was stirred in 8 ml of dry benzene, at the following temperatures for the times stated:

$CH_2{=}CH{-}CH_2Cl$	temp. 20–25°	time 1 h
$CH_3{-}CH{=}CH{-}CH_2Br$	20–25°	1 h
$C_6H_5{-}CH{=}CH{-}CH_2Cl$	60–65°	2 h
$C_6H_5{-}CH_2Cl$	70°	1 h
C_6H_5I	60°	0.5 h

The dark-orange mixture was then filtered and the solvent removed *in vacuo*. The product, which was normally an oily paste, was washed several times with n-hexane and with benzene/n-hexane mixtures until a solid powder was obtained. The same operations could not be performed for bis(1-cyano-4-penten-1-yl)nickel which was soluble in n-hexane.

Bis(1-cyano-4-penten-1-yl)nickel. See ref. 1.

Bis(1-cyano-4-hexen-1-yl)nickel. (Found: C, 60.32; H, 7.46; N, 10.10; Ni, 22.20.

$C_{14}H_{20}N_2Ni$ calcd.: C, 61.18; H, 7.28; N, 10.20; Ni, 21.38 %.) IR spectrum ($CHCl_3$): 2220 (s, $C{\equiv}N$), 1450 (m), 1437 (m), 1379 (w, δ_s CH_3), 1112 (vw), 965 [s, δ(CH-*trans*)], 912 (w) cm^{-1}. NMR spectrum (Relative to tetramethylsilane as internal standard; τ is referred to centre of multiplet.), τ: 9.5, 8.85, 8.4, 7.9, 4.6 ppm. Approximate relative intensity: 1:2:3:2:2.

From thermal decomposition at 140–180°, and vapour phase chromatographic separation of products and their thin-layer chromatographic purification, *cis,trans*-2,5-heptadienenitrile, *trans,trans*-2,5-heptadienenitrile and *trans*-5-heptenenitrile were isolated. Treatment with dry hydrogen chloride in benzene gave only *trans*-5-heptenenitrile.

Bis(1-cyano-5-phenyl-4-penten-1-yl)nickel. (Found: C, 72.49; H, 6.33; N, 6.92; Ni, 14.85. $C_{24}H_{24}N_2Ni$ calcd.: C, 72.40; H, 6.02; N, 7.01; Ni, 14.72 %.) IR spectrum (nujol, CS_2): 2220 (s, $C{\equiv}N$), 1593 [w, ν(C=C)], 1575 [vw, ν(C=C)], 1490 [w, ν(C=C)], 1066 (w), 1028 (w), 977 (w), 960 [s, δ(CH-*trans*)], 738 [s, δ(CH aromatic)], 689 [s, δ(CH aromatic)] cm^{-1}. NMR spectrum, τ: 9.34, 8.58, 7.55, 3.65, 2.75 ppm. Approximate relative intensity: 1:2:2:2:5.

Thermal decomposition at 150–180°, and isolation of products as before, gave *trans,trans*-6-phenyl-2,5-hexadienenitrile and *trans*-6-phenyl-5-hexenenitrile. Treatment with dry hydrogen chloride in benzene gave only *trans*-6-phenyl-5-hexenenitrile.

Bis(1-cyano-3-phenylpropyl)nickel. The yield was too low and the elemental analysis could not be carried on. IR spectrum (nujol): 2220 (s, $C{\equiv}N$), 1961 [vw, δ(CH)], 1872 (vw), 1802 (vw), 1598 [w, ν(C=C)], 1523 (vw), 1498 [m, ν(C=C)], 1338 (vw), 1075 (w), 1028 (w), 748 [s, δ(CH aromatic)], 697 [s, δ(CH aromatic)] cm^{-1}. NMR spectrum, τ: 8.78, 8.12, 7.25, 2.8 ppm. Approximate relative intensity: 1:2:2:5. Treatment with dry hydrogen chloride in benzene gave 4-phenylbutanenitrile.

Bis(1-cyano-2-phenylethyl)nickel. The yield was too low and the elemental analysis could not be carried on. IR spectrum (nujol): 2220 (s, $C{\equiv}N$), 1961 [vw, δ(CH)], 1872 [vw, δ(CH)], 1802 [vw, δ(CH)], 1680 (vw), 1598 [w, ν(C=C)], 1523 (vw), 1498 [m, ν(C=C)], 1075 (w), 1028 (w), 750 [s, δ(CH aromatic)], 699 [s, δ(CH aromatic]) cm^{-1}. NMR spectrum τ: 9.30, 7.88, 2.88 ppm. Approximate relative intensity: 1:2:5. Treatment with dry hydrogen chloride in benzene gave 3-phenylpropanenitrile.

Bis[1-cyano-3-(3-phenylisoxazolin-5-yl)propyl]nickel. Benzonitrile oxide (250 mg), dissolved in benzene (5 ml), was added to bis (1-cyano-4-penten-1-yl) nickel dissolved in benzene (5 ml); the mixture was stirred at 50° for 1 h. After removal of the solvent *in vacuo*, addition of n-hexane caused the precipitation of a brown solid, which was purified repeatedly by dissolution in benzene and precipitation with n-hexane. (Found: Ni, 13.1. $C_{28}H_{26}N_4O_2Ni$ calcd.: Ni, 11.9 %.) Vinyl bands were absent from the IR spectrum ($C{\equiv}N$, 2220 cm^{-1}).

Treatment with dry HCl in benzene gave 3-phenyl-5-(4-cyanobutyl)isoxazoline, m.p. 68° (crystallized from methanol/water) (Found: C, 73.0; H, 6.55. $C_{13}H_{14}N_2O$ calcd.: C, 73.3; H, 6.40 %.) The IR spectrum and m.p. are identical with those of a sample prepared by reaction of 5-hexenenitrile with benzonitrile oxide.

Reaction of allyl bromide with bisacroleinnickel. Allyl bromide (2.1 g) was added to a suspension of bisacroleinnickel (2.4 g) in benzene. The mixture was stirred for 10 minutes at room temperature and then filtered. The red-brown solution was evaporated *in vacuo*. From the residue, on mild heating, a red solid sublimed. By IR spectrography it was shown to be π-allylnickel bromide. Further work for the characterization of the residue is in progress.

^{14}C acrylonitrile. ^{14}C acrylonitrile was prepared by dehydration of ^{14}C 3-hydroxypropanenitrile cyanohydrin with sodium formate at 180–220°.

Reaction (3) with ^{14}C acrylonitrile. The reaction was performed on a mixture of allyl bromide (480 mg), bisacrylonitrilenickel (650 mg) and ^{14}C acrylonitrile (239 mg) in benzene. Bis(1-cyano-4-penten-1-yl)nickel was decomposed by hydrogen chloride and 5-hexenenitrile was separated by gas chromatography. Specific activity of ^{14}C acrylonitrile 2.16 μc/mmole; specific activity calculated for a complete exchange of bis-acrylonitrilenickel with acrylonitrile 0.77 μc/mmole. Specific activity of 5-hexenenitrile 0.80 μc/mmole.

π-Allylbromo(triphenylphosphine)nickel. Allyl bromide (250 mg) was added to a suspension of bisacrylonitrile(triphenylphosphine)nickel (650 mg) in benzene (10 ml); the mixture was stirred at 20° for half an hour and then filtered. The solvent was removed *in vacuo*. The diamagnetic, red-orange solid was crystallized from benzene/hexane. (Found: C, 57.22; H, 4.83; Br, 17.5. $C_{21}H_{20}NiPBr$ calcd.: C, 57.1; H, 4.53; Br, 18.3%.)

In the same way π-allylchloro(triphenylphosphine)nickel was prepared. It was identical with the compound described by Heck *et al.*[10].

ACKNOWLEDGEMENTS

The authors wish to thank Prof. A. Quilico and Prof. G. P. Chiusoli for their interest and the helpful discussions.

SUMMARY

The preparation is reported of the class of compounds with elementary formula $[R'\text{-}CH_2\text{-}CH(CN)]_2Ni$ where R' is $CH_2{=}CH\text{-}CH_2$, $CH_3\text{-}CH{=}CH\text{-}CH_2$, $C_6H_5\text{-}CH{=}CH\text{-}CH_2$, $C_6H_5\text{-}CH_2$, or C_6H_5. A polymeric structure involving C–Ni bonds and C≡N–Ni coordination is suggested for these complexes. Some properties of the compounds are described and the mechanism of their formation is discussed.

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