Hydrocyanation and Hydrogenation of Acetylenes catalysed by Cyanocobaltates

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Acetylenes are regioselectively hydrocyanated by cyanocobaltate prepared at CN : Co < 5 : 1 to give saturated secondary nitriles *via* unsaturated nitriles without the use of hydrogen cyanide, and partly hydrogenated to olefins or saturated hydrocarbons. In the presence of 2,2′-bipyridyl, hydrogenation of acetylene predominates, reflecting the formation of a highly active hydride complex $[Co(CN)_3(bipy)H]^-$. The preliminary formation of a $[\pi\text{-acetylene–}Co(CN)_4]^{3-}$ complex is assumed to explain the fact that the complex is active only at CN : Co < 5 : 1. Hydrocyanation is explained by the reductive coupling of the vinyl and cyano ligands of $[\sigma\text{-vinyl–}Co(CN)_5]^{3-}$ which is formed by the reaction of the π-acetylene complex, rather than acetylene itself, with $[Co(CN)_5H]^{3-}$.

Pentacyanocobaltate(II) $[Co(CN)_5]^{3-}$ exhibits a variety of reactions with organic and inorganic compounds.[1] The high reactivity results from the inorganic radical character of the complex, but reactions of the cyano-ligand have not been observed. The reaction between cyanocobaltate and acetylene thus far reported is the formation of bridged dimeric complexes, $[(CN)_5CoC(R)=C(R')Co(CN)_5]^{6-}$, between $[Co(CN)_5]^{3-}$ and acetylenes (RC≡CR′; R, R′ = H, CN, CO_2Me, and CO_2Et),[2] but we have found that nitriles are formed from acetylene catalysed by cyanocobaltate. The reaction is a new type of hydrocyanation which proceeds without the use of hydrogen cyanide. Since there has been little study of the hydrocyanation of acetylenes,[3] we have examined the utility of the reaction as a method of synthesizing nitriles from acetylenes. In the chemistry of catalysis by transition metal complexes, it is important to clarify the mechanism of formation or cleavage of the carbon–carbon and carbon–hydrogen bonds, but the mechanism of hydrocyanation with the use of hydrogen cyanide has not been clarified. The present reaction is performed by an experimentally simple procedure and is useful for the elucidation of mechanism for hydrocyanation. In a previous report,[4] we proposed the intermediate formation of $[\sigma\text{-vinyl–}Co(CN)_5]^{3-}$ by the direct reaction of acetylene with $[Co(CN)_5H]^{3-}$, but the mechanism is not sufficient to explain that hydrocyanation proceeds only at CN : Co < 5 : 1. We reconsider the mechanism by reference to our result that the cyanation of vinyl halides by cyanocobaltate also proceeds only at CN : Co < 5 : 1 by the mechanism involving $[Co(CN)_4]^{3-}$ as the active species.[5]

On the other hand, although $[Co(CN)_5H]^{3-}$ is well known as a catalyst for the hydrogenation of conjugated olefins,[1,6] its involvement in the hydrogenation of acetylenes has not been known. We here report that acetylenes are effectively hydrogenated by $[Co(CN)_3(bipy)H]^-$ which is prepared at CN : Co < 5 : 1 in the presence of 2,2′-bipyridyl.

Results

Table 1 shows the results of hydrocyanation and hydrogenation of acetylenes catalysed by cyanocobaltate. Both reac-

Table 1. Hydrocyanation and hydrogenation of acetylenes by cyanocobaltate[a]

RC≡CR′ R	R′	[RC≡CR′]/[Co]	*t*/h	H_2 (cm³)	Conv.[b] (%)	Yield[c] (%)	Product composition (%) RCH(CN)-CH_2R'	RC(CN)=CHR′	RCH=CHR′	RCH_2-CH_2R'
cyclo-$C_6H_{10}(OH)$[d]	H	1	10	86	100	96 (84)	85	0	15	0[e]
		1[f]	24	0	0	0				
		1.5[g]	24	134	98	95 (87)	82	0	18	0
		2	24	71	59	40	83	0	17	0
$Me_2C(OH)$	H	1	10	82	100	85 (71)	98	0	2	0[h]
		2	10	21	77	31	51	44	5	0
EtC(Me)(OH)	H	1	10	97	100	95 (84)	93	0	7	0[i]
		2	10	33	58	28	67	28	5	0
Ph	H	1	24	98	100	40 (20)	91[j]	0	0	9
		2	24	40	70	12	58[k]	9	11	23
Ph	Me	1	24	0	2	1	86[l]	5[l]	10	0
$PhCH_2CH_2$	H	1	24	8	12	6	77	12	11	0

[a] $[Co]_0$ 0.2M, CN : Co = 4.9 : 1, at 45 °C, in 25 cm³ H_2O, 1 atm H_2. [b] Mol % based on added acetylenes, determined by g.l.c. analysis. [c] Total g.l.c. and isolated (in parentheses) yields based on added acetylenes. [d] 1-Ethynylcyclohexanol. [e] Cyclohexanone (<1%) was detected. [f] CN : Co = 6.0. [g] Acetylene was added in portions. [h] Composition of hydrogenolysed products in gaseous phase (%): $H_2C=CHCH(Me)_2$ (2), $Me_2C=CHMe$ (98). [i] Composition of hydrogenolysed products in gaseous phase (%): $H_2C=CH(Me)Et$ (4), *trans*- and *cis*-MeCH=C(Me)Et (45 and 51), HC≡CH(Me)Et (1). [j] PhCH(CN)Me (68) + $PhCH(CONH_2)Me$ (23). [k] PhCH(CN)Me (34) + $PhCH(CONH_2)Me$ (24). [l] $PhCH(CN)CH_2Me$: $PhCH_2CH(CN)Me$: PhC(CN)=CH(Me) : PhCH=C(CN)Me = 94 : 2 : 2 : 3.

Table 2. Hydrocyanation and hydrogenation of acetylenes by cyanocobaltate in the presence of 2,2′-bipyridyl [a]

RC≡CR′						Product composition (%)		
R	R′	t/h	H_2 (cm^3)	Conv.[b] (%)	Yield[c] (%)	RCH(CN)-CH_2R'	RCH=CHR′	RCH_2-CH_2R'
cyclo-C_6H_{10}(OH)	H	5	113	100	98 (88)	7	93	0
Ph	H	2	198	100	85 (70)	24	0	76
Ph	Me	5	0	3	3	36	64	0
$PhCH_2CH_2$	H	5	28	30	26 (20)	17	83	0

[a] $[Co]_0$ 0.2M, CN : Co : bipy = 3.5 : 1 : 1, [RC≡CR′] : [Co] = 1, at 45 °C, in 25 cm^3 H_2O-MeOH (1 : 1 v/v), 1 atm H_2. [b] Based on added acetylenes, estimated by g.l.c. analysis. [c] G.l.c. and isolated (in parentheses) yields based on added acetylenes.

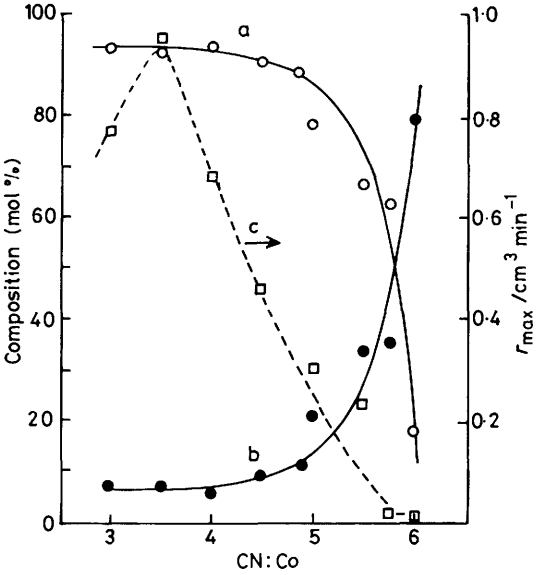


Figure. Effect of the CN : Co ratio in the presence of 2,2′-bipyridyl in the reaction of 1-ethynylcyclohexanol: a, cyclo-$C_6H_{10}(OH)CH=CH_2$; b, cyclo-$C_6H_{10}(OH)CH(CN)CH_3$; c, maximum rates of the hydrogen absorption. $[Co]_0$ = $[acetylene]_0$ = 0.2M, $[bipy]_0$ 0.2M, in 25 cm^3 H_2O-MeOH (1 : 1), at 45 °C and 1 atm H_2

tions proceeded only at CN : Co < 5 : 1, and hydrocyanation was the predominant reaction. γ-Hydroxyacetylenes gave good yields of saturated secondary nitriles, but reactivities of other acetylenes, especially internal and alkyl-substituted terminal acetylenes, were fairly low. When the concentration of added acetylene was greater than that of the cobalt complex, the reaction was sluggish, gave lower yields of products, and unsaturated nitriles were detected. However, the addition of acetylenes in portions was required when reactions involving more than stoicheiometric amounts of acetylenes were performed. Hydrogenolysed products (olefins) were also formed from 3-methylbut-1-yn-3-ol and 3-methylpent-1-yn-3-ol, but not from 1-ethynylcyclohexanol which gave a small amount of cyclohexanone (<1%). In the reaction of phenylacetylene, the yield of products was much less than that expected from the conversion, suggesting that phenylacetylene may be trapped in aqueous solution by forming a fairly stable complex. We have attempted to detect the complex by n.m.r. spectroscopy, but ^1H n.m.r. spectroscopy was not useful probably because only deuteriated complexes can be formed in the reaction in D_2O. The complexes decomposed during measurement of a ^{13}C n.m.r. spectrum. The reactivity of PhC≡CMe was very low, yielding mainly $PhCH(CN)CH_2Me$, but small amounts of $PhCH_2CH(CN)Me$ and (*E*)-PhCH=C(CN)Me were detected, suggesting that hydrocyanation proceeds by a *cis*-1,2-addition mechanism.

The effect of the reaction temperature was studied for the reaction of 1-ethynylcyclohexanol. The maximum rate of absorption of hydrogen increased with increasing temperature without affecting the yield and composition of products. The rate was first order rather than second order with respect to the initial concentration of the cobalt complex ($[Co]_0$ 0.075—0.2M, $[1\text{-ethynylcyclohexanol}]_0$ 0.075M, 45 °C).

The effect of addition of 2,2′-bipyridyl was studied in water–methanol as solvent. As shown in Table 2, hydrogenation of acetylenes took place predominantly. The Figure shows the effect of the CN : Co ratio on catalytic activity and composition of products in the reaction of 1-ethynylcyclohexanol. Hydrogenation proceeded predominantly at CN : Co < 5 : 1 and the reactivity of acetylene estimated by the rate of the hydrogen absorption was a maximum at CN : Co = 3.5 and decreased with the increasing CN : Co ratio. After an initial rapid conversion of phenylacetylene, the reaction became slow and the slow period became longer with an increasing concentration of the acetylene. Addition of acetylene by portions was also effective in performing the reaction at more than stoicheiometric amounts of acetylene.

Discussion

Hydrocyanation of olefins with hydrogen cyanide is catalysed by transition metal complexes and used industrially for synthesis of nitriles, but the reaction mechanism has been little studied.[7] The proposed mechanism [equations (1)—(7)] involves a H–M–CN complex as the active species and an intermediate σ-alkyl–M–CN complex which may be converted into nitrile either by addition of another molecule of HCN [equations (4)—(6)] or by a reductive elimination process [equation (7)].

$$\text{M} + \text{HCN} \rightleftharpoons \text{H—M—CN} \quad (1)$$

$$\text{H—M—CN} + \text{olefin} \rightleftharpoons \text{H—M}(\pi\text{-olefin})\text{CN} \quad (2)$$

$$\text{H—M}(\pi\text{-olefin})\text{CN} \longrightarrow \sigma\text{-alkyl—M—CN} \quad (3)$$

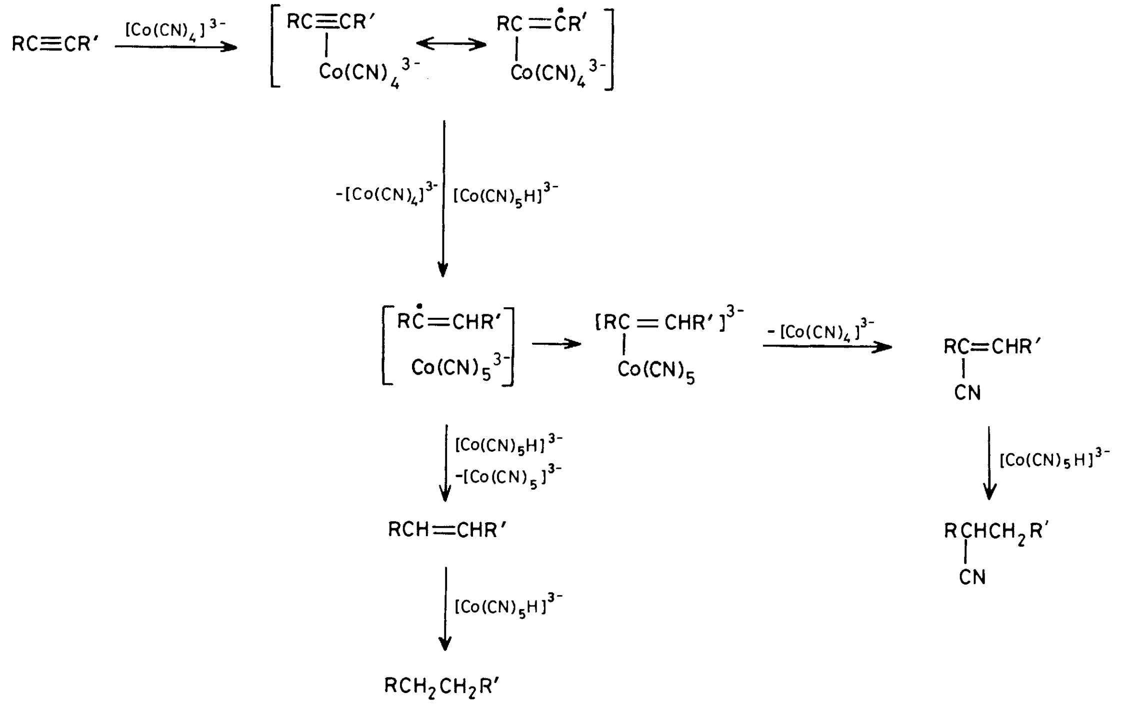
$$\sigma\text{-alkyl—M—CN} + \text{HCN} \longrightarrow \sigma\text{-alkyl—M(CNH)CN} \quad (4)$$

$$\sigma\text{-alkyl—M(CNH)CN} \longrightarrow \sigma\text{-alkyl—C(=NH)—M—CN} \quad (5)$$

$$\sigma\text{-alkyl—C(=NH)—M—CN} \longrightarrow \text{H—M—CN} + \text{alkyl—CN} \quad (6)$$

$$\sigma\text{-alkyl—M—CN} \longrightarrow \text{M} + \text{alkyl—CN} \quad (7)$$

Since $[Co(CN)_5H]^{3-}$, which is formed by the reaction of $[Co(CN)_5]^{3-}$ with hydrogen, has a H–Co–CN linkage, it is expected that the complex could be used for hydrocyanation of olefins without the use of hydrogen cyanide, but we found that not olefin but acetylene is hydrocyanated by the complex. The method is very useful for synthesis of saturated secondary



Scheme.

nitriles from terminal acetylenes, especially from γ-hydroxyacetylenes. The initial products, acrylonitriles, cannot be obtained in high yields, because they are rapidly hydrogenated. For synthetic purposes, the use of a larger amount of catalyst is advantageous rather than the reaction of greater than stoicheiometric amounts of acetylenes. Compared with cyanation with the use of hydrogen cyanide, the present method is very effective for reasons of experimental simplicity, *e.g.* easy preparation of catalyst under hydrogen and ready isolation of the products from the aqueous solvents.

Previously we have proposed a mechanism which assumes that [σ-vinyl-$Co(CN)_5]^{3-}$ is formed by the direct 1,2-addition of $[Co(CN)_5H]^{3-}$ to acetylene and the σ-complex is a common intermediate for both hydrocyanation and hydrogenation. However, the mechanism cannot explain the fact that both reactions proceed only at CN : Co < 5 : 1, because $[Co(CN)_5H]^{3-}$ is formed both at CN : Co < 5 : 1 and > 5 : 1. Since this characteristic effect of the CN : Co ratio suggests the participation of $[Co(CN)_4]^{3-}$ as an important active species,[5] we propose the Scheme, which involves the pre-formation of a [π-acetylene–$Co(CN)_4]^{3-}$ complex, for the following reasons. (1) $[Co(CN)_4]^{3-}$, which is formed by equation (8), at CN : Co < 5 : 1,[8] can activate substrates by one-electron-transfer.[5,9] (2) Formation of a π-acetylene complex with low-valent transition metal complexes is well known.[10] It is very probable that acetylene forms a π-complex with $[Co(CN)_4]^{3-}$, which forms the stable [π-olefin–$Co(CN)_4]^{3-}$.[9] (3) An η^2-acetylene ligand is known to be activated to η^1-acetylene with some radical character.[10] $[Co(CN)_5H]^{3-}$, which reacts readily with a radical, will react with the η^1-acetylene ligand to form the σ-vinyl complex, while regenerating $[Co(CN)_4]^{3-}$. When formation of carbon–carbon and cobalt–carbon bonds occurs simultaneously or stepwise in the solvent cage, the formation of the σ-vinyl complex will proceed as a *cis*-1,2-addition. When the timing of the combination of the vinyl radical and Co^{II} is such as to permit the reaction of the radical with $[Co(CN)_5H]^{3-}$, hydrogenation will take place. (4) The fact that hydrogenation proceeds predominantly in the presence of 2,2′-bipyridyl is due to $[Co(CN)_3(bipy)H]^-$ which has a weaker Co–H bond than $[Co(CN)_5H]^{3-}$.[11] The first hydrogen transfer to the η^1-acetylene ligand will take place rapidly, but [σ-vinyl-$Co(CN)_3(bipy)]^-$, if formed, must be less stable than [σ-vinyl-$Co(CN)_5]^{3-}$. The second hydrogen transfer will be facilitated with $[Co(CN)_3(bipy)H]^-$ rather than $[Co(CN)_5H]^{3-}$. (5) Clear n.m.r. evidence for formation of a σ-vinyl complex and the reductive coupling of the vinyl and cyano ligands of the complex to form unsaturated nitriles with regenerating $[Co(CN)_4]^{3-}$ were shown in the cyanation of vinyl halides.[5] This process is applicable to the present reaction and must be a rate-determining step. This is consistent with the rapid hydrogenation of unsaturated nitriles and with the first-order dependence of the rate on the cobalt concentration in the reaction of 1-ethynylcyclohexanol. (6) The reaction of the σ-vinyl complex with $[Co(CN)_5H]^{3-}$ is less probable because σ-vinyl complexes are formed even in the presence of $[Co(CN)_5H]^{3-}$.[5]

$$\begin{tikzcd} {[Co(CN)_5]^{3-}} \arrow[r, shift left, "H_2"] & {[Co(CN)_5H]^{3-}} \arrow[l, shift left] \arrow[r, shift left, "OH^-"] & {[Co(CN)_5]^{4-}} \arrow[l, shift left] \arrow[d, shift left, "-CN^-"] \\ & & {[Co(CN)_4]^{3-}} \arrow[u, shift left] \end{tikzcd} \qquad (8)$$

The result that hydrocyanation proceeds more readily with γ-hydroxyacetylenes than others suggests the co-ordination of acetylenes also with the hydroxy group, because hydrogenolysed products are formed from these acetylenes.[12] On the other hand, inhibition of the reaction by addition of greater than stoicheiometric amounts of acetylenes suggests the formation of a stable cobaltacyclopentadiene complex,[10] but we have not confirmed the structure.

The important characteristics of nitrile synthesis catalysed by cyanocobaltate, *i.e.* hydrocyanation of acetylene and cyanation of vinyl[5] and aryl[13] halides, are that the low-valent species, $[Co(CN)_4]^{3-}$, plays an important role as a one-electron-transfer reagent to activate substrates and that nitriles are formed by the reductive coupling of the *sp*^{2} carbon and cyano ligands co-ordinated to the cobalt atom. The facts that neither olefins are hydrocyanated by cyanocobaltate nor nitriles are formed from $[\sigma\text{-alkyl–}Co(CN)_5]^{3-}$ seems to suggest that the nitrile formation by the reductive coupling of a σ-alkyl–M-CN complex [equation (7)] may not be involved in the hydrocyanation of olefins catalysed by metal complexes with the use of hydrogen cyanide.[7,14]

Experimental

An aqueous solution of cyanocobaltate was prepared by mixing $CoCl_2$ (5 mmol, 0.649 g) and KCN (variable; in typical cases, 24.5 mmol, 1.595 g) in water (25 cm^3) at 45 °C under hydrogen. In the case of bipyridylcyanocobaltate, 2,2′-bipyridyl (5 mmol, 0.780 g) was added and H_2O–MeOH (1 : 1 v/v) was used as a solvent. After pre-absorption of hydrogen, the acetylene (5 or 10 mmol) was added, and the reaction was followed by measuring the hydrogen absorption and by g.l.c. analysis of the dichloromethane extract of small portions of the solution. Pink precipitates were formed as observed with the cyanation of vinyl halides.[5] Products were extracted with dichloromethane, concentrated *in vacuo*, and distilled bulb-to-bulb by using a Kugelrohr apparatus (Büchi's Glass Tube Oven GKR-50). Pure products were obtained by preparative g.l.c. and identified by elemental analysis, and i.r. and ^{1}H and ^{13}C n.m.r. spectroscopy. Typical examples follow. 1-Ethynylcyclohexanol (5 mmol, 0.64 cm^3) was completely converted within 10 h at 45 °C, and $C_6H_{10}(OH)CH(CN)CH_3$ (85%), $C_6H_{10}(OH)CH{=}CH_2$ (15%), and a small amount of cyclohexanone (<1%) were formed. The nitrile was distilled at 60 °C and 0.1 mmHg to give an oil (0.55 g), $\nu_{max.}$ (neat) 2 230 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.32 (d, 3 H), 1.59 (m, 10 H), 2.39 (s, 1 H), and 2.66 (q, 1 H); δ_C ($CDCl_3$) 12.0 (q), 21.5 (t), 25.3 (t), 34.7 (t), 34.9 (t), 37.8 (d), 71.5 (s), and 121.5 p.p.m. (s, CN). The acetylene (15 mmol) was completely converted when it was added in portions, but the reactivity was very low when it was added all at once. 3-Methylbut-1-yn-3-ol (5 mmol, 0.49 cm^3) yielded almost selectively the saturated nitrile, but butenes were also formed in the gas phase. When 10 mmol of the acetylene was added, formation of an unsaturated nitrile was observed. $Me_2C(OH)CH(CN)CH_3$ had $\nu_{max.}$ (neat) 2 240 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.33 (d, 3 H), 1.36 (s, 3 H), 2.38 (s, 1 H), and 2.68 (q, 1 H); δ_C ($CDCl_3$) 13.2 (q), 26.8 (q), 38.2 (d), 71.0 (s) and 121.7 p.p.m. (s, CN). $Me_2C(OH)C(CN){=}CH_2$ had $\nu_{max.}$ (neat) 2 220 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.49 (s, 6 H), 1.92 (s, 1 H), 5.92 (s, 1 H), and 6.07 (s, 1 H); δ_C ($CDCl_3$) 28.9 (q), 71.5 (s), 117.6 (s), 125.2 (s), 127.6 (t, J_{CH} 163.6 Hz), and 131.6 p.p.m. (s). 3-Methylpent-1-yn-3-ol (5 mmol, 0.57 cm^3) reacted in the same manner as 3-methylbut-1-yn-3-ol, and gave quantitatively $EtC(Me)(OH)CH(CN)CH_3$, which was a mixture of stereoisomers (2 : 3), $\nu_{max.}$ (neat) 2 240 cm^{-1} (C≡N); δ_H ($CDCl_3$) 0.97 (t, 6 H), 1.27 (s, 6 H), 1.31 (d, 3 H), 1.34 (d, 3 H), 1.62 (t, 4 H), 1.85 (s, 2 H), 2.72 (q, 1 H), and 2.75 (q, 1 H); δ_C ($CDCl_3$) 7.68 (q), 12.6 (q), 13.0 (q), 23.2 (q), 23.6 (q), 32.0 (t), 32.2 (t), 36.4 (d), 36.8 (d), 72.86 (s), 72.93 (s), and 121.7 p.p.m. (s, CN). When 10 mmol of the acetylene was added, an unsaturated nitrile, $EtC(Me)(OH)C(CN){=}CH_2$, was isolated, $\nu_{max.}$ (neat) 2 220 cm^{-1} (C≡N); δ_H ($CDCl_3$) 0.91 (t, 3 H), 1.45 (s, 3 H), 1.72 (s, 1 H), 5.99 (s, 1 H), and 6.07 (s, 1 H); δ_C ($CDCl_3$) 7.7 (q), 27.1 (q), 33.6 (t), 74.9 (s), 117.6 (s, CN), 128.8 (t, J_{CH} 164.2 Hz), and 130.3 p.p.m. (s). Hydrogenolysis products (olefins) were also detected in the gaseous phase. Phenylacetylene (5 mmol, 0.54 cm^3) reacted very slowly, and the yield of products, which were identical with those obtained from the cyanation of α-bromostyrene,[5] was lower than that expected from complete conversion. When 10 mmol of phenylacetylene was added, the solution became yellow-orange and heterogeneous, and formation of styrene was observed, indicating that the catalytic cycle to form $[Co(CN)_5H]^{3-}$ was inhibited. The saturated nitrile, PhCH(CN)Me, was converted partly into $PhCH(CONH_2)Me$ in the prolonged reaction. β-Methylphenylacetylene (5 mmol, 0.62 cm^3) scarcely reacted, but a small amount of nitriles was detected. The main product was $PhCH(CN)CH_2Me$, but (*E*)-PhCH=C(CN)Me, which was also formed from (*E*)-PhCH=C(Me)Br,[5] and $PhCH_2CH(CN)Me$ were also detected. $PhCH(CN)CH_2Me$ had $\nu_{max.}$ (neat) 2 230 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.06 (t, 3 H), 1.93 (dq, 2 H), 3.73 (t, 1 H), and 7.33 (s, 5 H); δ_C ($CDCl_3$) 11.5 (q), 29.1 (t), 38.8 (d), 120.7 (s, CN), 127.2 (d), 127.9 (d), 128.9 (d), and 135.7 p.p.m. (s). $PhCH_2CH(CN)Me$ had $\nu_{max.}$ (neat) 2 230 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.30 (d, 3 H), 2.81 (d, 2 H), 2.83 (m, 1 H), and 7.28 (s, 5 H); δ_C ($CDCl_3$) 17.5 (q), 27.4 (d), 39.9 (t), 122.3 (s, CN), 127.1 (d), 128.6 (d), 128.9 (d), and 139.7 p.p.m. (s). 4-Phenylbut-1-yne (5 mmol, 0.7 cm^3) also scarcely reacted, but a small amount of a saturated nitrile was obtained. $PhCH_2CH_2CH(CN)Me$ had $\nu_{max.}$ (neat) 2 230 cm^{-1} (C≡N); δ_H ($CDCl_3$) 1.33 (d, 3 H), 1.96 (m, 2 H), 2.57 (m, 1 H), 2.79 (m, 2 H), and 7.25 (s, 5 H); δ_C ($CDCl_3$) 18.0 (q), 24.9 (d), 33.2 (t), 122.7 (s, CN), 126.3 (d), 128.3 (d), 128.6 (d), and 140.1 p.p.m. (s).

Acknowledgements

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