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Reactivity of 2-methyl-3-butenenitrile in the presence of catalytic amounts of various cobalt complexes in ionic liquid

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Abstract

The behavior of 2-methyl-3-butenenitrile (2M3BN) in the presence of catalytic amount of several cobalt complexes was evaluated. Irrespective of the nature of cobalt complexes and the experimental conditions (presence of ligand [such as $P(OPh)_3$ or pyridine], or/and of Lewis acid [$ZnCl_2$, $AlCl_3$], organic solvent or ionic liquid), the product of isomerization 2-methyl-2-butenenitrile was obtained instead of the expected rearranged product 3-pentenenitrile (3PN). This result was explained by the activation of C─H bond instead of C─CN bond. With 3PN, the first example of a reversible cleavage of the C─CN with complex derived from Co^+ was evidenced.

Keywords: Pentenenitrile; Cobalt complexes; Ionic liquid

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1. Introduction

The rearrangement of 2-methyl-3-butenenitrile (2M3BN) into 3-pentenenitrile (3PN), the second step in the preparation of the adiponitrile, is often chosen as a model reaction in order to determine the catalytic performance of new ligands [1,2] or new media, such as ionic liquid [3,4]. Besides, this conversion occurring through a C─CN bond cleavage (Fig. 1a), there is a possible isomerization of 2M3BN into the side product, 2-methyl-2-butenenitrile (2M2BN) which forms via C─H activation (Fig. 1a).

The nickel(0) complexes clearly give the best results and the mechanism of the reaction of rearrangement of 2M3BN into 3PN with Ni^0 catalyst (Fig. 1a) has been studied extensively [5–8]. This mechanism is based on a $Ni^0 \leftrightarrow Ni^{2+}$ equilibrium. However, some authors claimed that cobalt complexes such as $Co_2(CO)_8$, $Hg[Co(CO)_4]_2$ and $HCo[(P(OAr)_3]_4$ $\{Ar = C_6H_5, o\text{-}CH_3C_6H_4\}$ present, for this reaction, analogous results to those of Ni^0 [9–13].

Recently, we reported this catalytic rearrangement in the presence of phosphine complexes Ni^0, in biphasic ionic liquid/organic solvent. Several neutral and ionic phosphines and ionic liquids have been tested. The best results in the conversion of 2M3BN (96%) and selectivity to 3PN (93%) were obtained for the catalytic system associating $Ni(cod)_2$, (*m*-sulfophenyl)-diphenylphosphine sodium salt, [TPPMSNa] as the ligand and 1-butyl-2,3-dimethylimidazolium-bis(trifluoromethylsulfonyl)imide [BMMIm][NTf_2] as the ionic liquid, in a biphasic ionic liquid/heptane solvent system. Partition experiments proved that the catalyst was immobilized in the ionic phase. TON (1020) and TOF (103 h^{-1}) of the catalyst were measured [3,4]. Recycling of the catalyst is possible but leads to an important deactivation which is related to the evolution of the nature of the ligand by ion exchange between the cation (Na^+) of the ligand and the cation [$BMMIm^+$] of the ionic liquid. This exchange induces a change in the nature of the ligand, thereby altering the nature of the catalyst and of the catalytic activity [14].

To immobilize a catalyst into ionic liquid, the catalyst ought to be ionic. Another approach is to use the ionic catalytic precursor in which the charge is on the metal center and with neutral ligand [15–20].

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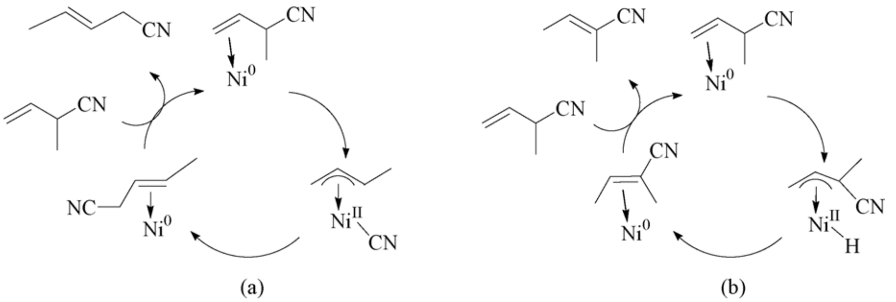
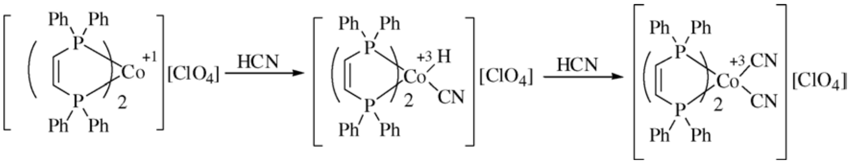


Fig. 1. Mechanism of rearrangement in the presence of Ni^0 of 2M3BN into (a) 3PN via a C—CN activation; (b) 2M2BN via a C—H activation.

In this paper, we report our attempts to realize the rearrangement 2M3BN into 3PN with a series of ionic cobalt complexes in the oxidation state Co^{1-}, Co^{1+} and even Co^0. The Co^{1-} complex is isoelectronic with Ni^0. On the other hand, the cationic complex Co^{1+} such as $[(Ph_2CH{=}CHPPh_2)_2Co]^+[ClO_4]^-$, seems to be a possible candidate for this reaction due to the fact it reacts with HCN to give the cationic complex Co^{3+} [21]:



2. Results

2.1. Synthesis of cobalt complexes

Several cobalt complexes $(PPh_3)_3CoCl$ [22], 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridinecobaltmethyl, (BIP)-CoMe [23], 1,1,1-tris(diphenyl-phosphinomethyl)ethane cobalt chloride, P_3CoCl [24], $HCo(P(OPh)_3)_4$, $NaCo(CO)_4$ [25], $[Co(pyridine)_6][Co(CO)_4]_2$ [26], $(\eta^3allyl)Co(CO)_2PPh_3$ [27] and $H[Co\{P(OPh)_3\}_4]$ [28,29] have been synthesized according to the procedure available in the literature.

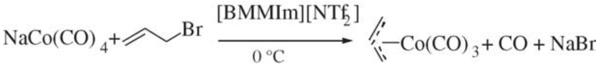
The reaction of $(PPh_3)_3CoCl$ with $Li(N(SO_2CF_3)_2$, $(LiNTf_2)$, in the presence of bidentate phosphines, using the same procedure as for the anion ClO_4^- [30], gave the cationic complexes $[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$ and $[(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$:

$$(PPh_3)CoCl + LiNTf_2 + 2\,Ph_2PCH_2CH_2PPh_2 \xrightarrow{EtOH} [(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$$

$$(PPh_3)CoCl + LiNTf_2 + 2\,Ph_2PCH{=}CHPPh_2 \xrightarrow{EtOH} [(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$$

The reaction of P_3CoCl with $NaCo(CO)_4$ afforded the complex $[P_3Co]^+[Co(CO)_4]^-$ (30% yield) which was characterized by electron spray ionization (ESI): cationic mode, 683 $[P_3Co^+]$, 711 $(P_3Co^+ + CO)$, 739 $(P_3Co^+ + 2CO)$; and anionic mode, 171 $[Co(CO)_4^-]$.

The synthesis of $(\eta^3allyl)Co(CO)_3$ has been realized using the ionic liquid, $[BMMIm][NTf_2]$, as the solvent, instead of ether, as described in the literature [27], allowing to isolate and purify in *only one step*, $(\eta^3allyl)Co(CO)_3$ by sublimation, directly from the reaction mixture (50% yield):



2.2. Catalytic experiments

The catalytic experiments were run as in the already published work [3,4]. In a glove bag, a mixture of 2M3BN (distilled over activated molecular sieves (3 Å) before use), cobalt complexes (2M3BN/[Co] = 200) and ionic liquid $[BMMIm][NTf_2]$ (2 g) were introduced into a stirred reaction vessel or in Carousel tubes (equipped with an external cooler to avoid incorrect mass balance) for 3 h at 100 or 150 °C. The reactor was cooled down to room temperature and the products were analyzed by gas chromatography. Different protocols for work-up analysis were tested. Distillation of volatile organic products under dynamic vacuum and dilution of reaction medium with tetrahydrofuran and direct injection into a gas chromatograph afforded good results in terms of analysis. In all cases, at 100 °C as well as at 150 °C, no other organic compounds were detected in GC.

All cobalt complexes $(PPh_3)_3CoCl$, (BIP)CoMe, P_3CoCl, $(\eta^3allyl)Co(CO)_3$, $(\eta^3allyl)Co(CO)_2PPh_3$ and $[P_3Co]^+[Co(CO)_4]^-$, $[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$, $[(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$, $HCo(P(OPh)_3)_4$, $NaCo(CO)_4$, $Co_2(CO)_8$ and $CpCo(CO)_2$ were tested in the catalytic conditions. Irrespective of the nature of cobalt complexes and the experimental conditions (in the presence or absence of ligand $[P(OPh)_3$ or pyridine], in the presence or absence of Lewis acid $[ZnCl_2$, $AlCl_3]$, organic solvent or ionic liquid), the rearrangement of 2M3BN into 3-pentenenitrile (3PN) was not observed, and the double bond shift product 2-methyl-2-butenenitrile (2M2BN) was generally the main product, Table 1.

Table 1
Results of the reaction of 2M3BN in the presence of catalytic amount of cobalt complexes in $[BMMIm][NTf_2]$

Complex	*T* (°C)	Conv. 2M3BN	Select. 2M2BN	Mass balance	Aspect
$(PPh_3)_3CoCl$	100	0	0	100	Dark green + Co metal
$(PPh_3)_3CoCl + AlCl_3$	100	0	0	100	Dark green + Co metal
$PPh_3)_3CoCl + BF_3{\cdot}OEt_2$	100	0	0	100	Dark green + Co metal
$(PPh_3)_3CoCl + 5PPh_3$	100	0	0	100	Dark green
$(PPh_3)_3CoCl + 5PPh_3$	150	20	20	100	Dark green + Co metal
$(PPh_3)_3CoCl + 5P(OPh)_3$	150	24	25	95	Green-brown
$[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$	100	0	0	100	Green
$[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$	150	40	20	79	Green
$[(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$	150	65	50	89	Brown
$(\eta^5\text{-}C_5H_5)Co(CO)_2$	150	100	86	84	Red
$(BIP)CoBr_2 + {}^\circ Zn$	150	99	85	86	
$Co_2(CO)_8$	150	68	50	78	Orange + Co metal
$Co_2(CO)_8$ + pyridine	150	80	80	100	Orange
$Co_2(CO)_8 + 5P(OPh)_3$	150	99	75	75	Dark orange
$NaCo(CO)_4$	100	91	87	92	Clear brown
$NaCo(CO)_4 + 5P(OPh)_3$	100	100	76	78	Orange
$NaCo(CO)_4 + 5P(OPh)_3$	150	100	100	94	Clear brown

Conditions: Co complex (0.036 mmol), 2M3BN (0.650 g, ca. 6.2 mmol) and $[BMMIm][NTf_2]$ (2.0 g) were stirred for 3 h at 100 or 150 °C. The products of the reaction were analyzed by gas chromatography (see Section 4). (Commercial 2M3BN contains (79% 2M3BN, 12% *trans*-2M2BN, 6% *cis*-2PN and 2% *trans*-3PN.) Mass balance ≠ 100% due to the effect of the work-up, no other organic compounds have been detected.

The complex $(PPh_3)_3CoCl$ was not active at 100 and 150 °C even in the presence of Lewis acid and most of the complex was transformed in Co particles. In the presence of an excess of ligand ($L = PPh_3$, $P(OPh)_3$), the conversion in 2M2BN was around 20%. With $[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$ and $[(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$, the conversion of 2M3BN occurred only above 150 °C. With $Co_2(CO)_8$, alone or in the presence of pyridine or $P(OPh)_3$, the conversion in 2M2BN increased with temperature. With $NaCo(CO)_4$, the conversion of 2M2BN was total at 100 °C.

Note that in order to compare these results with Dupont' work on cobalt, we reproduced rigorously the same experimental conditions as those depicted in Dupont' patent, we did not observe any rearrangement of 2M3BN into 3PN (Table 2).

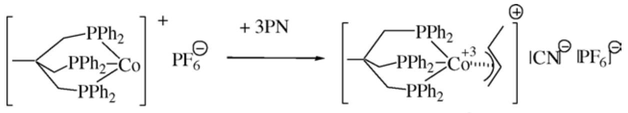
In conclusion, the rearrangement of 2M3BN into 3PN is not observed with cobalt complexes whatever be our experimental conditions.

2.3. Stoichiometric reaction

The key step in the rearrangement of 2M3BN into 3PN is the activation of the C–CN bond and the formation of the $(\eta^3\text{allyl})Ni(CN)L_n$ intermediate (Fig. 1a [5–8]), while the isomerization of 2M3BN into 2M2BN occurs via C–H activation (Fig. 1b). The competitive C–C and C–H bond activation reactions in the isomerization of allylcyanide by Ni^0 catalyst was recently reported [6]. This study demonstrates clearly that the C–H activation induces the formation of conjugated nitrile [6]. Our results suggest that with all cobalt complexes the C–H bond activation is favored.

One example of cleavage of the C–CN bond with cobalt complexes is described in the case of stoichiometric reaction of alkyl and arylnitrile with $[(Ph_3P)_3CoN_2]Li$ [32]. Nevertheless, with allyl cyanide there is rearrangement into crotonitrile [32].

The stoichiometric reaction of 2M3BN with the complex $[P_3Co]^+[PF_6]^-$ yielded quantitatively 2M2BN. On the contrary, the stoichiometric reaction of $[P_3Co]^+[PF_6]^-$ with 3-pentenenitrile afforded a green paramagnetic compound, **2**, fully characterized as a (η^3-crotyl) complex by ESI spectroscopy: cationic mode 738 ($P_3Co((\eta^3\text{-crotyl})^+$) and ^{31}P NMR (CD_3NO_2): 42, −27 (free ligand), −144 ($PF_6{}^-$). Thus, there is activation of the C–CN bond, and consequently, formation of the Co^{3+} complex $[P_3Co^{3+}(\eta^3\text{-crotyl})(CN)][PF_6]$. Note that generally, the reaction of $[P_3Co]^+[PF_6]^-$ with several diene and heterodiene provides $[P_3Co^{1+}(\eta^4\text{-diene})]^+[PF_6]^-$ complexes [24].



1 **2**

At 60 °C, **2** was spontaneously and quantitatively transformed into the starting material. In this case, the formation of conjugated nitrile 2PN was not observed, contrarily to the complex $[(Ph_3P)_3CoN_2]Li$, which induced isomerization of allyl cyanide into crotonitrile [32].

On one hand, **2**, in the presence of 3PN, $ZnCl_2$ and HCN, was decomposed (blue product $P_3Co^{2+}(CN)_2$ derivative) and gave 10% of valeronitrile and no dinitrile derivatives.

On the another hand, no allylcyanide was formed during the reaction of HCN (under acetone cyanohydrin state) on $(\eta^3\text{allyl})Co(CO)_3$ and $(\eta^3\text{allyl})Co(CO)_2PPh_3$ (standard experimental conditions of hydrocyanation reaction, experimental conditions).

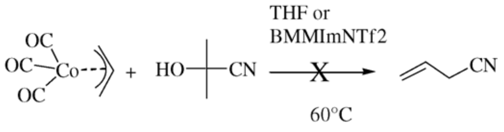
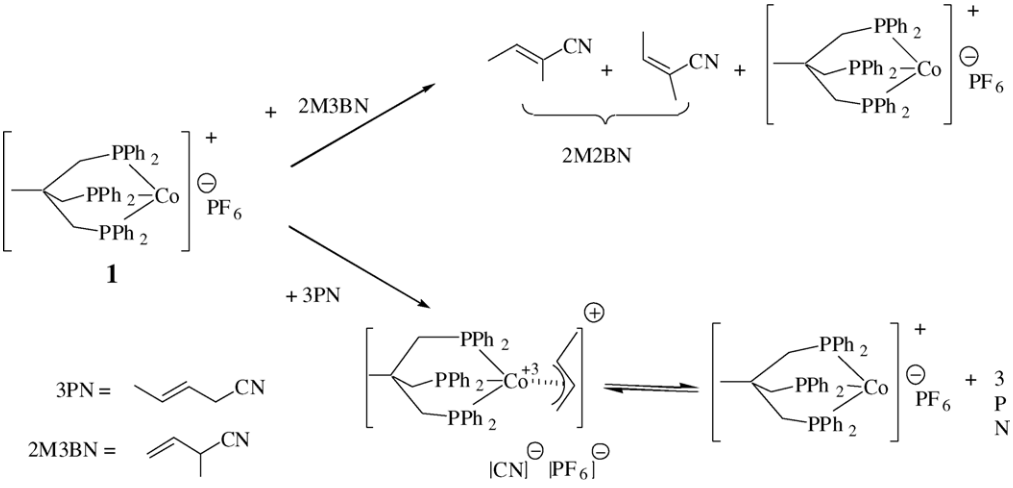


Table 2
Results of the catalytic rearrangement reaction of 2M3BN following the procedure depicted in Dupont' patent

Catalyst	*T* (°C)/*t* (h)	Amount of 3PN present in the starting 2M3BN (%)	Amount of 3PN present in the reactional mixture at the end of the reaction (%)
$CoCl_2$ (10 mmol); $P(OPh)_3$ (40 mmol); Al (3 mmol); 2M3BN (250 mmol)	130/9	8.32 1.5	17.3[a] 1.5[b]
$CoCl_2$ (10 mmol); $P(OPh)_3$ (40 mmol); Zn (5 mmol); 2M3BN (250 mmol)	120/9	8.32 1.5	16.1[a] 1.7[b]
$CoCl_2$ (10 mmol); $P(OPh)_3$ (40 mmol); Zn (5 mmol); 2M3BN (250 mmol)	130/9	8.32 1.5	17.3[a] 1.9[b]
$HCo(P(OPh)_3)_4$ (5 mmol); $CoCl_2$ (5 mmol); 2M3BN (25 mmol)	120/22	? 1.5	7.56[a] 1.5

[a] Ref. [31].
[b] Our work.

These results indicate that the reductive elimination to form pentenenitrile seems to be not feasible with Co^{1+} precursors. The formation of 3PN from **2** could be due to the fact that the CN group was probably not directly bonded to the cobalt center, as in the case of $HNiL_4{}^+CN^-$ [33]. The formation of 3PN would be the result of nucleophilic attack of the ion CN^- on (η^3-crotyl) group. This was confirmed by the fact that 3PN was also obtained when KCN was added to a solution of **2**.



3. Conclusion

Several cobalt complexes in the oxidation states −1, 0, +1, synthesized $(PPh_3)_3CoCl$, $[(Ph_2PCH_2CH_2PPh_2)_2Co]^+[NTf_2]^-$, $[(Ph_2PCH{=}CHPPh_2)_2Co]^+[NTf_2]^-$, P_3CoCl, (BIP)CoMe, (η^3allyl)$Co(CO)_3$, (η^3allyl)$Co(CO)_2PPh_3$, $[P_3Co]^+[Co(CO)_4]^-$, $HCo(P(OPh)_3)_4$, $NaCo(CO)_4$, commercial $Co_2(CO)_8$ and $CpCo(CO)_2$ were tested in the catalytic reaction of rearrangement of 2M3BN. Irrespective of the nature of cobalt complexes and the experimental conditions (presence of ligand [$P(OPh)_3$ or pyridine], or/and of Lewis acid [$ZnCl_2$, $AlCl_3$], organic solvent or ionic liquid), only the thermodynamically more stable 2-methyl-2-butenenitrile was obtained instead of 3PN. The same result was obtained when we have repeated the Dupont' patent procedures. It has been demonstrated that, in our standard experimental conditions, the rearrangement of 2M3BN into 3PN, does not occur in the presence of catalytic or stoichiometric amounts of cobalt complexes.

Most of the results could be interpreted by an easier C–H versus C–C bond activation with all cobalt complexes. However, with 3PN, the first example of a reversible cleavage of the C–CN with cationic Co^{1+}, $[P_3Co]^+[PF_6]^-$ was observed with the formation of $[P_3Co(\eta^3\text{-crotyl})[CN][PF_6]$. At 60 °C, the 3PN was re-obtained, without isomerization into 2PN, probably through a nucleophilic attack of the CN^- on the crotyl group and not via a reductive elimination as with Ni^0.

4. Experimental

$CoCl_2 \cdot 6H_2O$, zinc powder, 3-pentenenitrile, triphenylphosphine, $CoBr_2$ and MeMgBr were purchased from Aldrich and used without further purification. $Li(N(CF_3SO_2)_2)$ was purchased from Solvionic and used as received.

Solvents were distilled using the appropriate drying agents: CaH_2 for acetonitrile and dichloromethane, K_2CO_3 for chloroform and acetone, sodium for toluene and sodium/benzophenone for diethylether and tetrahydrofuran. 2-Methyl-3-butenenitrile was purchased from Rhodia Research Center, distilled from P_2O_5 and stored under argon.

4.1. Solution NMR

^{1}H, ^{13}C and ^{31}P NMR were recorded on a Bruker AC 300 MHz spectrometer. Chemical shifts were measured relative to residual protons and carbons of the solvent for ^{1}H and ^{13}C, respectively. Positive ^{31}P chemical shifts are downfield from external 85% H_3PO_4. CD_2Cl_2 was purchased from SDS, distilled over CaH_2 and degassed before use. THF-d_8 was obtained from Aldrich and used without further treatments.

4.2. ^{1}H and ^{13}C solid NMR

Solid state NMR spectra were recorded on a Bruker DSX-300 Spectrometer equipped with a standard 4 mm double-bearing probe head and operating at 75.47 and 300.18 MHz for ^{13}C and ^{1}H, respectively. ^{13}C NMR spectra were recorded as follows: 30° pulse on ^{13}C nuclei, and acquisition under a 80 kHz decoupling field on protons, with 1 s recycle delay and 5 kHz spinning speed unless otherwise specified.

4.3. Mass spectrometry

Mass spectra were acquired on a ThermoFinnigan LCQ Advantage ion trap instrument, detecting positive (+) and negative (−) ions in the ESI mode. Samples (1–10 μg/mL in acetonitrile) were infused directly into the source (5 μL min^{-1}) using a syringe pump. The following source parameters were applied: spray voltage 3.0–3.5 kV, nitrogen sheath gas flow 5–20 arbitrary units. The heated capillary was held at 200 °C. MS spectra were obtained by applying a relative collision energy of 25–40% of the instrumental maximum.

4.4. Ionic liquids

1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [BMMIm][NTf2] has been prepared as described in the literature. It was purified by chromatography on classical neutral alumina (Fluka) and characterized by elemental analysis and NMR spectroscopy [34].

4.5. Synthesis

The complexes $(PPh_3)_3CoCl$ [22], 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineCoMe [23], $NaCo(CO)_4$ [25], (allyl)$Co(CO)_2(PPh_3)$, P_3CoCl [24] were synthesized according to literature procedure.

4.6. (η^3allyl)$Co(CO)_3$

This complex was already synthesized by the method reported by Heck, but its preparation was greatly simplified by using an ionic liquid. At 0 °C, under an argon atmosphere, allyl bromide (0.2 mL, 2.4 mmol) was added to a solution of $NaCo(CO)_4$ (0.51 g, 2.6 mmol) in 10 mL of [BMMI][NTf_2]. The orange solution became green and was stirred for 12 h. It was then distilled under vacuum to recover (allyl)$Co(CO)_3$ (0.2 g, 50% yield) as a slightly orange liquid. ^{1}H NMR (capillary tube): 5.47 (t, 1H), 3.61 (d, 2H), 2.72 (d, 2H). ^{13}C (capillary tube): 205, 82, 51.

4.7. [$P_3Co(\eta^3$-crotyl)(CN)][PF_6]

The complex P_3CoCl (P_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane) (0.4 g, 0.55 mmol) was dissolved in 20 mL of THF with $TlPF_6$ (0.192 g, 0.55 mmol). The solution was stirred under argon and after the formation of a white precipitate, 3-pentenenitrile (0.5 mmol) was added. The reaction medium stirred for 30 min. The solvent was removed under vacuum and the remaining solid extracted with dichloromethane (2 × 10 mL). After concentration under vacuum, a green powder could be isolated (0.25 g, 50% yield). Solid state ^{13}C NMR: 167, 130 (large peak), 69, 34, 26 (large peak). Liquid state ^{31}P NMR (CD_3NO_2): 42, −27 (free ligand), −144 (PF_6^-). ESI: cationic mode, 657 ($P_3O_2 + H^+$), 738 ($P_3Co((\eta^3$-crotyl)$^+$); and anionic mode, 145 (PF_6^-).

4.8. $[P_3Co]^+[Co(CO)_4]^-$

To a solution of P_3CoCl (0.192 g, 0.26 mmol) in 10 mL of THF $NaCo(CO)_4$ (52 mg, 0.26 mmol) was added under argon. The red solution was stirred for 2 h and then concentrated under vacuum. The red solid was extracted with CH_2Cl_2 (3 × 5 mL) in order to recover, after concentration under vacuum, a red powder (70 mg, 30% yield). ESI: cationic mode, 683 (P_3Co^+), 711 ($P_3Co^+ + CO$), 739 ($P_3Co^+ + 2CO$); anionic mode, 171 ($Co(CO)_4^-$).

4.9. $[(Ph_2PCH_2CH_2PPh_2)_2Co^{1+}][N(SO_2CF_3)_2]$

To a suspension of $(PPh_3)_3CoCl$ (1 g, 1.1 mmol) in 50 mL of ethanol, the ligand $Ph_2PCH_2CH_2PPh_2$ (1.3 g, 3.3 mmol) and $LiNTf_2$ (3.7 g, 13 mmol) was added. The solution is stirred under reflux for 3 h and then decanted at 0 °C. After filtration, the precipitate was washed with ethanol and dried under vacuum (1.2 g, 90% yield). ESI: cationic mode: 855 ($(Ph_2PCH_2CH_2PPh_2)_2Co^+$).

4.10. $[(Ph_2PCH{=}CHPPh_2)_2Co^{1+}][N(SO_2CF_3)_2]$

The ligand diphenylphosphinoethylene $Ph_2PCH{=}CHPPh_2$ (0.20 g, 0.5 mmol) and $LiNTf_2$ (0.13 g, 0.5 mmol) was added to a suspension of $(PPh_3)_3CoCl$ (0.22 g, 0.25 mmol). The reaction medium was stirred at 70 °C for 1 h before being decanted at 0 °C. After filtration, the green precipitate was washed with ethanol and dried under vacuum (0.22 g, 90%). ESI: cationic mode: 851 ($(Ph_2PCH{=}CHPPh_2)_2Co^+$), 455 ($(Ph_2PCH{=}CHPPh_2)_2Co^+$).

4.11. Catalytic experiments and analysis

Reactions were performed in a Carousel tube (parallel reactor "Radleys").

In a typical reaction, 0.036 mmol of cobalt complex (1 eq.), 0.650 mg of 2M3BN (220 eq.) and 2.0 g of $BMMImNTf_2$ were mixed under argon. The reaction medium was then heated for 3 h at 100 or 150 °C, and then cooled in liquid nitrogen.

Work-up: butylbenzene (100 mg) was added to the reaction mixture as an internal standard, reaction medium was then diluted with 10 mL of THF and a portion was directly injected into a gas chromatograph.

Analyses: The products were quantitatively analyzed by gas chromatography (HP6890 equipped with a TCD detector, Stabilwax-DA (polyethyleneglycol) column ($L = 30$ m, $\phi_{int} = 0.53$ mm, film thickness = 1 μm).

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