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Facile C–N bond cleavage mediated by electron-rich cyclopentadienyl cobalt(I) complexes[1]

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Abstract

The reaction of $[C_5H_5Co(PMe_3)_2]$ (**1**) with one equiv of $CNCH_2Ph$ leads to the formation of the substitution product $[C_5H_5Co(CNCH_2Ph)(PMe_3)]$ (**2**) which even at room temperature undergoes an intramolecular oxidative addition to give the isomer $[C_5H_5Co(CN)(CH_2Ph)(PMe_3)]$ (**4**). The corresponding Cp*Co derivative $[C_5Me_5Co(CN)(CH_2Ph)(PMe_3)]$ (**8**) is obtained from $[C_5Me_5Co(PMe_3)_2]$ (**5**) and $CNCH_2Ph$. In contrast to **2**, the analogous compound $[C_5H_5Co(CNTol)(PMe_3)]$ (**6**) is quite inert and does not react by N–C bond cleavage. The conversion of **2** to **4** in C_6D_6, acteone-d_6 and methanol-d_4 follows first order kinetics with a rate that is almost independent of the concentration of free PMe_3. Both **2** and **6** react with Ph_2CN_2 to give the *C,C*-bound ketenimine complexes $[C_5H_5Co(\kappa^2\text{-}C,C\text{-}Ph_2C{=}C{=}NR)(PMe_3)]$ (**9**, **10**) of which that with R = Tol rearranges thermally to the more stable *N,C*-bound isomer **11**.

Keywords: Cobalt; Isocyanide complexes; C–N bond cleavage; Ketenimine complexes

1. Introduction

Following our work on isocyanide cobalt(I) complexes of the general composition $[C_5H_5Co(CNR)(PMe_3)]$, which react with 1,2- and 1,3-dipoles to give four- and five-membered metallaheterocycles [1,2], we recently reported also on the reactivity of these half-sandwich-type compounds towards diazoalkanes [3] and arylazides [4]. In particular, the possibility to generate unsymmetrical carbodiimides such as $PhCH_2N{=}C{=}NPh$ from benzylisocyanide $PhCH_2NC$ and PhN_3 in the coordination sphere of cobalt prompted us to continue our investigations regarding the behavior of $[C_5H_5Co(CNCH_2Ph)(PMe_3)]$ (**2**) towards other substrates. In the course of these studies we observed that the starting material **2** as well as the in-situ formed C_5Me_5Co analogue is quite labile even in the absence of any reagent and undergoes facile $N–CH_2Ph$ bond cleavage. In this paper we describe the characterization of the respective products and discuss the kinetic data of the metal-assisted dissociation process.

2. Results and discussion

2.1. Preparation and rearrangement of isocyanide cobalt complexes

Using the electron-rich cyclopentadienyl complex **1** as the starting material, the isocyanide derivatives **2** and **3** are prepared by stepwise replacement of the phosphine ligands by benzylisocyanide. While **2** has been identified by analytical and spectroscopic techniques [4], the characterization of **3** turned out to be more difficult. The brown solid is extremely air-sensitive and

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[1] Dedicated to Professor R.B. King on the occasion of his 60th birthday.

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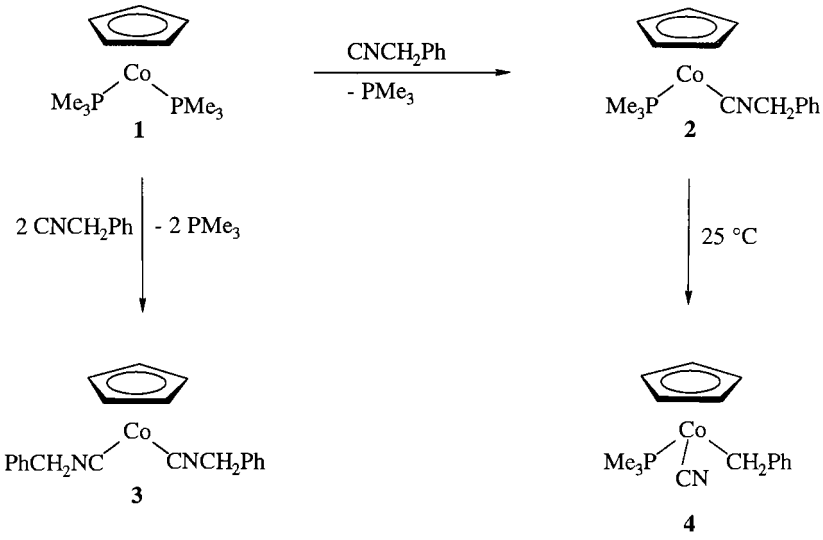


Scheme 1.

thus no correct elemental analysis could be obtained. The IR spectrum of **3** displays C≡N stretching frequencies at 2093, 1970 and 1935 cm^{-1}, i.e. at similar positions as found for other $[C_5H_5Co(CNR)_2]$ complexes [5]. The ^{1}H-NMR data are also consistent with the structural proposal shown in Scheme 1 and deserve no further comments.

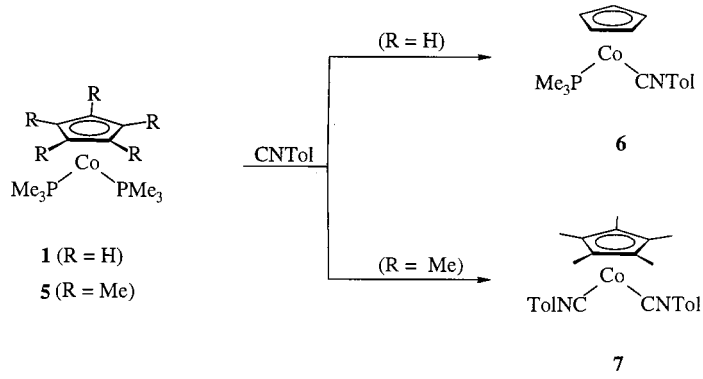
Compound **2**, which has already been used as precursor for the synthesis of ketenimine cobalt derivatives [4], is thermally rather labile and undergoes an isomerization to the benzyl(cyano)cobalt(III) complex **4** even at room temperature. After stirring a solution of **2** in benzene for 12 h, **4** has been isolated as an orange, only slightly air-sensitive solid in 83% yield. The most typical spectroscopic features of **4** are the intense ν(C≡N) stretch at 2082 cm^{-1} in the IR and the two signals (corresponding to the AB part of an ABX spin system) at δ 2.67 and 2.53 for the benzylic CH_2 protons in the ^{1}H-NMR spectrum.

In contrast to **2**, the related 4-tolylisocyanide complex **6** (Scheme 2) does not rearrange in solution to the cobalt(III) isomer $[C_5H_5Co(CN)(4\text{-}C_6H_4Me)(PMe_3)]$. Compound **6**, which has been obtained from equimolar amounts of **1** and CNTol in benzene/pentane, is an orange, very air-sensitive solid decomposing already at 34°C. The corresponding Cp*Co derivative $[C_5Me_5Co(CNTol)(PMe_3)]$ could not be prepared from $[C_5Me_5Co(PMe_3)_2]$ (**5**) and CNTol since the first step of this process (replacement of one PMe_3 by CNTol) is quickly followed by the second one and thus the bis(isocyanide) compound **7** is obtained. By using a molar ratio of **6**/CNTol = 1/2, the yield of **7** is 83%. The IR spectrum of **7** displays three ν(C≡N) bands at 2063, 2032 and 1920 cm^{-1} which are shifted to somewhat lower frequencies compared to those of the CpCo complex **3**. Like **6**, compound **7** is also stable in solution and does not react to a $Co(CN)(4\text{-}C_6H_4Me)$ isomer.

However, an extremely facile N–C bond cleavage occurs on treatment of **5** with benzylisocyanide. If a solution of **5** and $CNCH_2Ph$ in benzene/ether is stirred at 0°C for 2–3 min, the benzyl(cyano)cobalt(III) complex **8** is formed and upon recrystallization from ether isolated as an orange solid in 74% yield. Apart from the IR spectrum, in which an intense C≡N stretching frequency appears at 2091 cm^{-1}, the NMR data of **8** are also in good agreement with the structural proposal depicted in Scheme 3. The ^{13}C-NMR spectrum displays two doublets at δ 138.2 and 12.4, which both show a strong P–C coupling and are assigned to the metal-bound CN and CH_2Ph carbon atoms, respectively. It should be mentioned that halfsandwich-type benzylcobalt(III) compounds of the general composition $[C_5H_5Co(CH_2Ph)(R)(PPh_3)]$ ($R = CH_3$, CH_2Ph) are known and have been prepared from $[C_5H_5CoI_2(PPh_3)]$ and Grignard reagents [6].

2.2. Kinetic studies

In order to find out along which mechanistic route the benzyl(cyano)cobalt(III) complexes **4** and **8** are formed, the kinetics of the reaction of **2** to **4** have been investigated. Since it seemed at least conceivable that ionic or radical intermediates are involved the rate measurements were performed in different solvents (C_6D_6, acetone-d_6 and methanol-d_4) and in the presence of radical scavengers such as cyclohexa-1.3-diene. The change in concentration of **2** and **4** during the runs was determined by ^{1}H-NMR spectroscopy. Fig. 1 shows a series of spectra which illustrate the decrease in concentration of **2** and the increase in concentration of **4** in C_6D_6 at room temperature. The most characteristic signals are those of the C_5H_5 protons at δ 4.75 (for **2**) and 4.15 (for **4**), of the benzylic CH_2 protons at δ 4.32

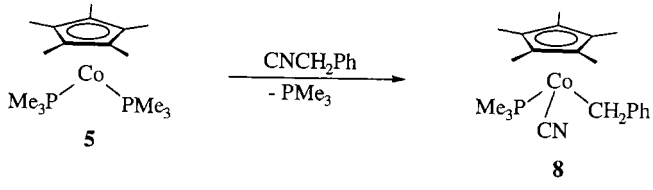


Scheme 2.

(for **2**) and 2.67 and 2.53 (for **4**), and of the PMe_3 protons at δ 1.03 (for **2**) and 0.93 (for **4**), respectively.

The plot shown in Fig. 2 reveals that the isomerization of **2** to **4** follows first-order kinetics. In C_6D_6 as the solvent, the rate constant k (Table 1) is almost independent of the presence of free PMe_3 and 1.3-C_6H_8, which indicates that in the rate-determining step a dissociation of the Co–PMe_3 bond does not occur and that radical intermediates are probably not involved [7]. The addition of ca. 15 equiv of CH_3OH to a solution of **2** in C_6D_6 leads to an increase of the rate constant by a factor of 2, which is consistent with the result that in methanol-d_4 as the solvent the rearrangement of **2** to **4** is about 10 times faster (at 25°C) than in C_6D_6. In acetone-d_6, the rate of the reaction is between that in C_6D_6 and CD_3OD, in agreement with the difference in polarity of the three solvents.

The relatively small difference in the rate constant k (and the half-life time $t_{\frac{1}{2}}$) for runs I, V and VI also rules out that in the rate-determining step ionic intermediates or ion-pairs such as $[C_5H_5Co(CN)(PMe_3)^+ PhCH_2^-]$ would be formed. Therefore, the most reasonable proposal for the mechanism of the isomerization of **2** to **4** is that an intramolecular oxidative addition occurs leading to the preservation of the Co–CN and the simultaneous formation of the new Co–CH_2Ph bond. In the transition state of the dissociative process possibly a $\delta+$ charge at the cobalt and a $\delta-$ charge at the benzylic CH_2 carbon atom is generated which could explain the small increase in the rate by going from C_6D_6 (run I) to acetone-d_6 (run V) and methanol-d_4 (run VI). As far as the reaction of **5** and $CNCH_2Ph$ is concerned, we assume that initially the isocyanide complex $[C_5Me_5Co(CNCH_2Ph)(PMe_3)]$ is formed which readily undergoes N–C bond cleavage to give **8**. The significantly greater rate of formation of **8** compared to **4** is probably due to the presence of the strong donor ligand C_5Me_5 which could stabilize a positive charge at the cobalt in the transition state much better than the unsubstituted C_5H_5 unit. With regard to the clean and quantitative formation of **4** from **2** it should be noted that various examples for the conversion of an isocyanide- to a cyano-metal compound are known [8] but in none of these reactions is the cleavage of the N–C bond accompanied by the generation of a new M–C linkage.



Scheme 3.

2.3. Preparation of C,C-bound and N,C-bound ketenimine cobalt complexes

Since we found that compound **2** reacts with phenyl- or 4-tolylazide to give carbodiimide cobalt derivatives [4], we were interested to find out whether related ketenimine cobalt complexes were accessible on a similar route. While on treatment of **2** with $PhCHN_2$ or $PhC(Me)N_2$ only decomposition of the diazoalkane occurs, the reaction of **2** with Ph_2CN_2 in acetone leads to a mixture of **4** and **9** (Scheme 4) with the latter as the dominating species. Upon fractional crystallization from ether, the ketenimine complex **9** was isolated as a brown, moderately air-sensitive solid in ca. 30% yield. The dihapto coordination of the $Ph_2C{=}C{=}NCH_2Ph$ ligand via both carbon atoms of the cumulene chain, which is already indicated by the strong C=C=N stretching frequency at 1695 cm^{-1} in the IR spectrum, is particularly supported by the NMR spectroscopic data. The ^{13}C-NMR spectrum of **9** displays the signals of the ketenimine carbon atoms =C= and CPh_2 at δ 208.7 and 11.4 which is in agreement with the data of other *C,C*-bound ketenimine metal derivatives [3,9].

The 4-tolylisocyanide complex **6** also reacts smoothly with diphenyldiazomethane but in this case only the ketenimine compound **10** (Scheme 4) is formed. On the basis of the IR and NMR spectroscopic data there is no

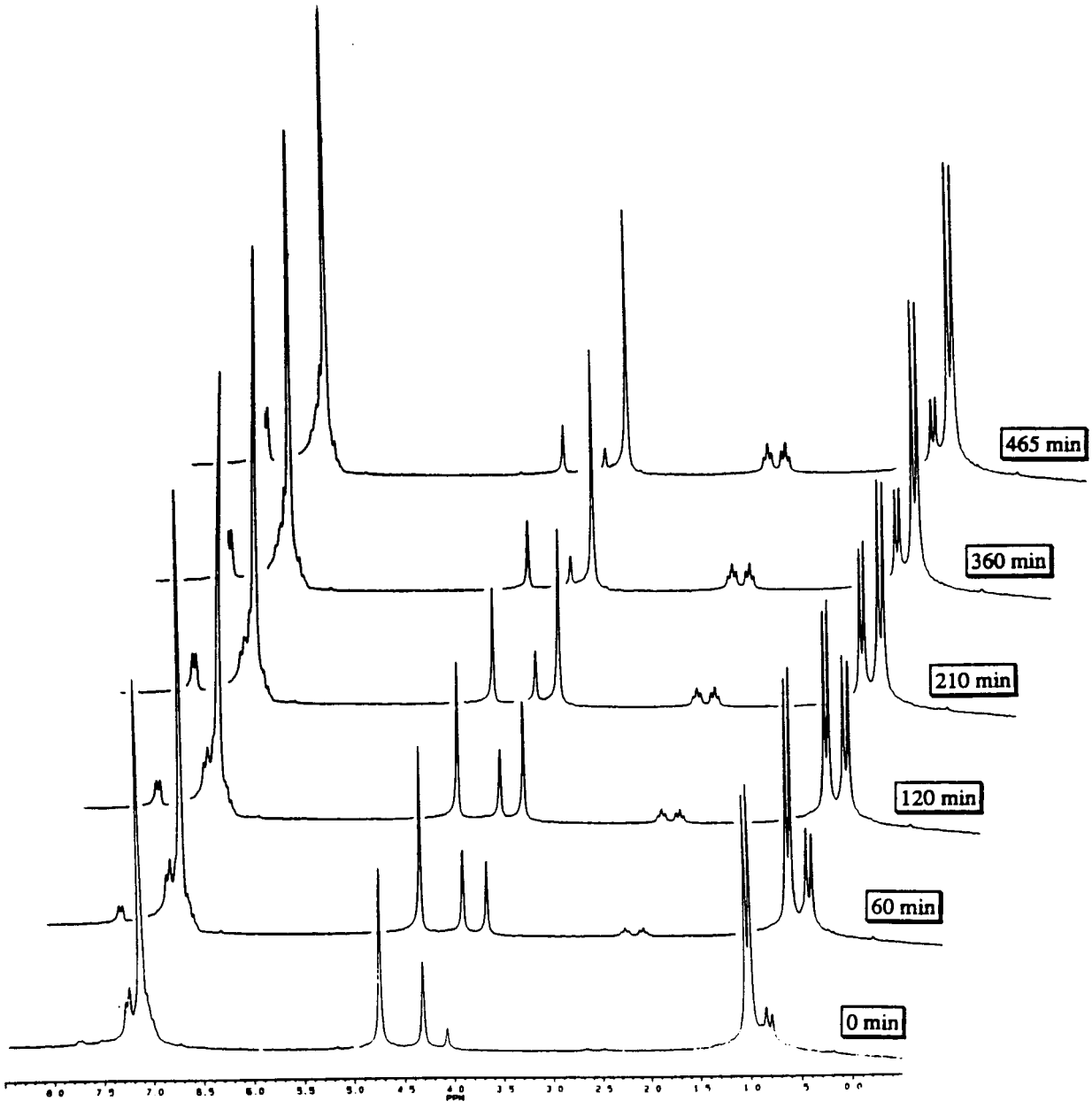


Fig. 1. ^{1}H-NMR spectra for the rearrangement of **2** to **4** in C_6D_6 (run I) at 25°C at different times.

doubt that the complexes **9** and **10** are structurally quite similar and that in the product which is initially generated from **6** and Ph_2CN_2 the ketenimine ligand Ph_2C=C=NTol is coordinated via both carbon atoms.

However, if a solution of **10** in benzene is heated at 50°C or irradiated with a UV lamp, a slow rearrangement to the *N*,*C*-bound isomer **11**, accompanied by partial decomposition of the starting material, takes place. The isomerization is facilitated in the presence of CH_3I, possibly due to a reversible addition of the alkyl halide to the ketenimine unit. Under these conditions, the isolated yield of **11** (which is a brown–orange solid) is 82%. The main differences in the spectroscopic data of isomers **10** and **11** are the ν(C=C=N) frequency in the IR spectrum, which for **11** is shifted by 65 cm^{-1} to lower wave numbers compared to **10**, the chemical shift of the signal of the PCH_3 protons in the ^{1}H-NMR spectrum (**10**: δ 0.17; **11**: δ 0.65), and most significantly the position of the resonances of the ketenimine carbon atoms in the ^{13}C-NMR spectrum. While for **10**, these signals appear at δ 212.7 and 11.2 as doublets, they are found at δ 161.2 (C=CPh_2) and 110.0 (C=CPh_2) in the spectrum of **11,** the latter resonance showing no P–C coupling. For a related ketenimine cobalt complex, of which the structure had been determined by X-ray crystallography, similar data were observed [3]. With regard to the mechanism of the isomerization of **10** to **11**, we assume that like for corresponding allene metal

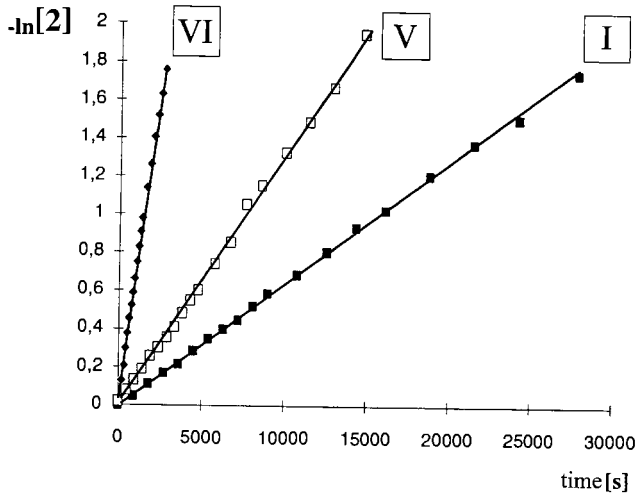


Fig. 2. Plot of -ln[**2**] vs time for the rearrangement of **2** to **4** in different solvents (I: in C_6D_6; V: in acetone-d_6; VI: in methanol-d_4).

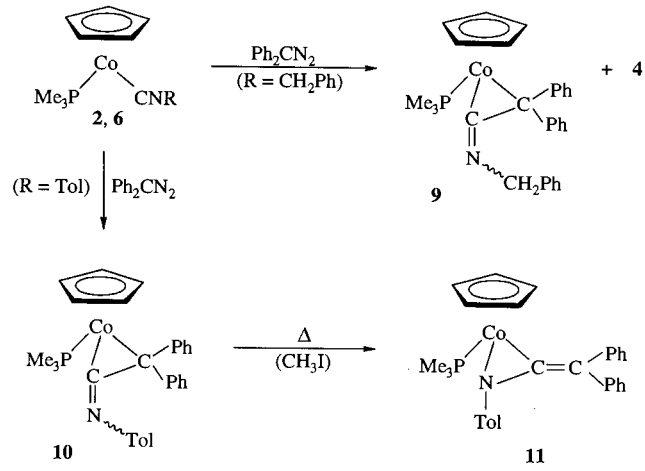
compounds [10] a slippage of the ketenimine unit along the N=C=C chain occurs which is driven by the steric requirements of the spectator ligands (C_5H_5 and PMe_3) and the aryl substituents of the Ph_2C=C=NTol moiety. In particular, in isomer **11** the steric hindrance between the phenyl groups at the terminal carbon atoms of the ketenimine and the cyclopentadienyl ring seems to be reduced which would be consistent with the higher thermodynamic stability of this species.

3. Experimental section

All reactions were carried out under argon and in carefully dried solvents. The starting materials $[C_5R_5Co(PMe_3)_2]$ (**1**, **5**) were prepared as described in the literature [11,12]; a preparative procedure for compound **2** was already given [4]. IR: Perkin-Elmer 1420; NMR: Varian EM 360 L, Jeol FX 90 Q, Bruker AMX 400. Melting and decomposition points were determined by DTA.

Table 1
Rate constants k (at 25 ± 1°C), half-life times $t_{\frac{1}{2}}$ and correlation coefficients r^2 for the reaction of **2** to **4** (run I: **2** in C_6D_6; run II: **2**+10 equiv of PMe_3 in C_6D_6; run III: **2**+1 equiv of 1.3-C_6H_8 in C_6D_6; run IV: **2**+15 equiv of CH_3OH in C_6D_6; run V: **2** in actone-d_6; run VI: **2** in methanol-d_4)

	k [s^{-1}]	$t_{\frac{1}{2}}$ [min]	r^2
I	6.29×10^{-5}	184	0.999
II	5.21×10^{-5}	222	1.000
III	5.99×10^{-5}	193	0.992
IV	1.22×10^{-4}	95	0.997
V	1.30×10^{-4}	89	0.999
VI	6.71×10^{-4}	17	0.997



Scheme 4.

3.1. Preparation of $[C_5H_5Co(CNCH_2Ph)_2]$ (**3**)

A solution of 336 mg (1.22 mmol) of **1** in 10 ml of benzene was treated with 3.70 ml of a 0.66 M solution (2.44 mmol) of $CNCH_2Ph$ in benzene at room temperature. A gradual change of color from dark-brown to red–brown occurred. After the solution was stirred for 5 min, the solvent was removed in vacuo and the oily residue was extracted with 20 ml of ether. The extract was filtered, the filtrate was concentrated to ca. 5 ml in vacuo, and then 5 ml of pentane was added. Storing the solution at -78°C for 12 h led to the formation of a brown, extremely air-sensitive solid. Yield 315 mg (72%). IR (C_6H_6): ν(C≡N) 2093, 1970, 1935 cm^{-1}. ^{1}H-NMR (60 MHz, C_6D_6): δ 7.18–6.88 (m; 10H; C_6H_5), 4.93 (s; 5H; C_5H_5), 4.11 (s, 4H, NCH_2).

3.2. Preparation of $[C_5H_5Co(CN)(CH_2Ph)(PMe_3)]$ (**4**)

A solution of 210 mg (0.66 mmol) of **2** in 5 ml of benzene was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the oily residue was recrystallized from benzene/pentane (1:5) to give orange, only slightly air-sensitive crystals. Yield 174 mg (83%); dec. temp. 106°C. Anal. Found: C, 60.77; H, 6.79; N, 4.36. Calc. for $C_{16}H_{21}CoNP$: C, 60.57; H, 6.67; N, 4.42. IR (KBr): ν(C≡N) 2082 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.77–7.06 (m; 5H; C_6H_5), 4.15 (s; 5H; C_5H_5), 2.67 and 2.53 (both dd; J(PH) = 7.7 and 6.6, J(HH) = 7.2 Hz, AB part of an ABX system; 2H; $CoCH_2$), 0.93 (d; J(PH) = 10.6 Hz; 9H; PMe_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 154.2 (d; J(PC) = 3.9 Hz; *ipso*-C of C_6H_5), 128.5, 128.4 and 123.7 (all s; C_6H_5), 88.6 (d; J(PC) = 1.0 Hz; C_5H_5), 17.1 (d; J(PC) = 31.1 Hz; PCH_3), 10.2 (d; J(PC) = 18.8 Hz; $CoCH_2$), signal of CN carbon atom not exactly located.

3.3. Preparation of $[C_5H_5Co(CNTol)(PMe_3)]$ (6)

A solution of 700 mg (2.53 mmol) of **1** in 10 ml of benzene was treated with 3.3 ml of a 0.77 M solution (2.53 mmol) of CNTol in pentane at room temperature. A quick change of color from dark-brown to red occurred. After the solution was stirred for 5 min, the solvent was removed in vacuo and the oily residue was extracted with 10 ml of pentane. Storing the extract for 12 h at −78°C gave an orange, very air-sensitive solid. Yield 660 mg (82%); dec. temp. 34°C. Anal. Found: C, 60.73; H, 6.73; N, 4.59. Calc. for $C_{16}H_{21}CoNP$: C, 60.57; H, 6.67; N, 4.42. IR (C_6H_6): ν(C≡N) 1825 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.18 and 6.85 (both d; J(HH) = 8.2 Hz; 2H each; C_6H_4), 4.77 (d; J(PH) = 1.2 Hz; 5H; C_5H_5), 2.02 (s; 3H; $C_6H_4CH_3$), 1.10 (d; J(PH) = 9.2 Hz; 9H; PMe_3).

3.4. Preparation of $[C_5Me_5Co(CNTol)_2]$ (7)

A solution of 529 mg (1.53 mmol) of **5** in 15 ml of ether was treated with 3.48 ml of a 0.88 M solution (3.06 mmol) of CNTol in pentane at 0°C. An immediate change of color from dark-brown to red occurred. The solution was worked-up as described for **6** to give red, extremely air-sensitive crystals. Yield 544 mg (83%); dec. temp. 68°C. Anal. Found: C, 74.02; H, 6.18; N, 6.27. Calc. for $C_{26}H_{29}CoN_2$: C, 72.88; H, 6.82; N 6.54. IR (C_6H_6): ν(C≡N) 2063, 2032, 1920 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.00 and 6.68 (both d; J(HH) = 7.8 Hz; 4H each; C_6H_4), 2.03 (s; 15H; C_5Me_5), 1.90 (s; 6H; $C_6H_4CH_3$). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 190.4 (s; CoCN), 134.8, 131.8, 130.0 and 124.6 (all s; C_6H_4), 93.9 (s; C_5Me_5), 21.0 (s; $C_6H_4CH_3$), 11.2 (s, $C_5(CH_3)_5$).

3.5. Preparation of $[C_5Me_5Co(CN)(CH_2Ph)(PMe_3)]$ (8)

A solution of 566 mg (1.63 mmol) of **5** in 10 ml of ether was treated at 0°C with 1.92 ml of a 0.85 M solution (1.63 mmol) of $CNCH_2Ph$ in benzene. After the solution was stirred for 2–3 min, the solvent was removed in vacuo and the oily residue was extracted with 10 ml of ether. The extract was filtered and the filtrate was concentrated to ca. 5 ml in vacuo. Storing the solution at −78°C for 12 h led to the formation of orange, only slightly air-sensitive crystals. Yield 467 mg (74%); dec. temp. 82°C. Anal. Found: C, 65.24; H, 8.42; N, 3.69. Calc. for $C_{21}H_{31}CoNP$: C, 65.11; H, 8.07; N, 3.62. IR (C_6H_6): ν(C≡N) 2091 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.78–7.07 (m; 5H; C_6H_5), 2.49 (d; J(PH) = 6.7 Hz; 2H; $CoCH_2$), 1.25 (d; J(PH) = 1.5 Hz; 15H; C_5Me_5), 0.89 (d; J(PH) = 9.8 Hz; 9H; PMe_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 151.7 (d; J(PC) = 2.5 Hz; *ipso*-C of C_6H_5), 138.2 (d; J(PC) = 37.8 Hz; CoCN), 130.4, 127.9 and 123.7 (all s; C_6H_5), 95.0 (s; C_5Me_5), 15.3 (d; J(PC) = 28.5 Hz; PCH_3), 12.4 (d; J(PC) = 18.8 Hz; $CoCH_2$), 9.5 (s; $C_5(CH_3)_5$).

3.6. Preparation of $[C_5H_5Co(\kappa^2\text{-}C,C\text{-}Ph_2C{=}C{=}NCH_2Ph)(PMe_3)]$ (9)

A solution of 350 mg (1.10 mmol) of **2** in 15 ml of acetone was treated with a solution of 214 mg (1.10 mmol) of Ph_2CN_2 in 5 ml of acetone at −78°C. After the solution was warmed to room temperature, it was stirred for 4 h and then the solvent was removed in vacuo. The residue was washed with 10 ml of pentane and subsequently extracted with 20 ml of ether. The extract was concentrated to ca. 10 ml in vacuo and after it was stored for 12 h at −78°C a brown solid was formed. Due to the ^{1}H-NMR spectrum, it consists of a 3:2 mixture of **9** and **4**. The solid was separated, the mother liquor was filtered, and the filtrate was concentrated to ca. 2 ml in vacuo. Cooling the concentrate to −78°C led to the formation of brown crystals, which were separated, washed with small portions of pentane (−20°C) and dried. Yield 153 mg (29%); dec. temp. 132°C. Anal. Found: C, 72.33; H, 6.89; N, 3.04. Calc. for $C_{29}H_{31}CoNP$: C, 72.04; H, 6.46; N, 2.90: IR (C_6H_6): ν(C=C=N) 1695 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.97–6.77 (m; 15H; C_6H_5), 5.53 and 5.33 (both d; J(HH) = 14.8 Hz; 1H each; NCH_2), 4.27 (d; J(PH) = 1.0 Hz; 5H; C_5H_5), 0.32 (d; J(PH) = 8.9 Hz; 9H; PMe_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 208.7 (d; J(PC) = 18.3 Hz; CoCN), 152.1 (d; J(PC) = 1.9 Hz; *ipso*-C of C_6H_5), 146.4 (d; J(PC) = 3.5 Hz; *ipso*-C of C_6H_5), 142.7 (s; *ipso*-C of C_6H_5), 129.8, 129.7, 129.1, 128.8, 128.2, 127.2, 126.8, 125.4 and 123.0 (all s; C_6H_5), 85.1 (d; J(PC) = 1.5 Hz; C_5H_5), 64.4 (d; J(PC) = 2.5 Hz; NCH_2), 19.2 (d; J(PC) = 28.2 Hz; PCH_3), 11.4 (d; J(PC) = 3.4 Hz; $CoCPh_2$).

3.7. Preparation of $[C_5H_5Co(\kappa^2\text{-}C,C\text{-}Ph_2C{=}C{=}NTol)(PMe_3)]$ (10)

Compound **10** was prepared as described for **9** starting from 517 mg (1.63 mmol) of **6** and 317 mg (1.63 mmol) of Ph_2CN_2. The reaction time was 7 h. Upon recrystallization of the oily residue from benzene/pentane (1:4) a brown–orange solid was obtained. Yield 374 mg (47%); dec. temp. 134°C. Anal. Found: C, 71.59; H, 6.55; N, 3.23. Calc. for $C_{29}H_{31}CoNP$: C, 72.04; H, 6.46; N, 2.90. IR (C_6H_6): ν(C=C=N) 1660 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.98–6.87 (m; 14H; C_6H_5 and C_6H_4), 4.33 (d; J(PH) = 1.0 Hz; 5H; C_5H_5), 2.27 (s; 3H; $C_6H_4CH_3$), 0.17 (d; J(PH) = 9.4 Hz; 9H; PMe_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 212.7 (d; J(PC) = 22.1 Hz; CoCN), 152.6 (d; J(PC) = 1.5 Hz; *ipso*-C of C_6H_5), 151.0 (d; J(PC) = 2.6 Hz; *ipso*-C of C_6H_5), 133.2, 129.4, 128.4, 127.2, 125.6, 123.1 and 122.3 (all s; C_6H_5 and C_6H_4), 86.5 (d; J(PC) = 1.3 Hz; C_5H_5),

21.1 (s; $C_6H_4CH_3$), 18.6 (d; $J(PC) = 28.5$ Hz; PCH_3), 11.2 (s, br; $CoCPh_2$).

3.8. Preparation of $[C_5H_5Co(\kappa^2\text{-}C,N\text{-}Ph_2C{=}C{=}NTol)(PMe_3)]$ (**11**)

A solution of 80 mg (0.17 mmol) of **10** in 10 ml of benzene was stirred, in the presence of 10 μl (0.16 mmol) of CH_3I, for 16 h at room temperature. The volatile components were removed in vacuo and the oily residue was recrystallized from ether/pentane (1:3). Upon storing the solution at -78°C, brown–orange crystals were obtained. Yield 66 mg (82%); dec. temp. 65°C. Anal. Found: C, 72.30; H, 6.74; N, 2.78. Calc. for $C_{29}H_{31}CoNP$: C, 72.04; H, 6.46; N, 2.90. IR (KBr): ν(C=C=N) 1630 cm^{-1}. ^{1}H-NMR (90 MHz, C_6D_6): δ 7.86–6.88 (m; 14H; C_6H_5 and C_6H_4), 4.28 (s; 5H; C_5H_5), 2.01 (s; 3H; $C_6H_4CH_3$), 0.65 (d; $J(PH) = 10.0$ Hz; 9H; PMe_3). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 161.2 (d; $J(PC) = 18.4$ Hz; CoCN), 150.2 and 145.4 (both s; *ipso*-C of C_6H_5), 139.8 (d; $J(PC) = 2.6$ Hz; *ipso*-C of C_6H_4), 132.1, 130.5, 129.6, 129.5, 129.4, 129.2, 128.1, 127.9, 127.2, 126.6, 125.6, 124.3, 124.1, 123.3 and 122.3 (all s; C_6H_5 and C_6H_4), 110.0 (s; CPh_2), 84.0 (d; $J(PC) = 2.0$ Hz; C_5H_5), 21.1 (s; $C_6H_4CH_3$), 16.6 (d; $J(PC) = 27.4$ Hz, PCH_3).

3.9. Kinetic studies

The rate measurements for the reaction of **2** to **4** were carried out with samples of **2**, which were recrystallized three times from pentane. The samples (5–20 mg) were dissolved under argon in a Glove box in an appropriate amount of C_6D_6, acetone-d_6 or methanol-d_4 to give 0.006–0.011 M solutions. For run II (see Table 1) ca. 10 equiv of PMe_3, for run III ca. one equiv of 1.3-C_6H_8, and for run IV ca. 15 equiv of CH_3OH were added. Each solution was transfered to an NMR tube (5 mm diameter), which was kept at -190°C and then sealed. Immediately after the tube was brought to room temperature, the NMR spectra were recorded. The kinetics were studied using a Bruker automation program implemented on a Bruker AC 200 NMR spectrometer. The delay between two consecutive data accumulations was set (D1) and the spectra were stored automatically. The total time increment between two measurements was the sum of the set delay D1 and the product of the number of scans (NS) and the aquisition time (AQ plus relaxation delay RD): $\tau = D1 + NS(AQ + RD)$, where $\tau = t_n - t_{n-1}$. For all measurements the temperature was 25 ± 1°C.

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