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Carbodiimide metal complexes and four-membered metallacycles from isocyanide metal precursors and aryl azides [1]

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Abstract

The reaction of $C_5H_5Co(CNR)(PMe_3)$ ($R = CH_2Ph$, C_6H_{11}) with aryl azides ArN_3 leads to a mixture of products with the carbodiimide complexes $C_5H_5Co(\kappa^2\text{-}C,N\text{-}RN{=}C{=}NAr)(PMe_3)$ (**3**, **4**) and the four-membered metallacycles $C_5H_5Co[\kappa^2\text{-}C,C\text{-}C(NR)N(Ar)C(NR)](PMe_3)$ (**5**, **6**) being the dominating species. For $R = C_6H_{11}$ and $Ar = C_6H_5$, an equilibrium between **6** and the isomer $C_5H_5Co[\kappa^2\text{-}C,C\text{-}C(NAr)N(R)C(NR)](PMe_3)$ (**7**) has been confirmed by NMR spectroscopy. Treatment of $C_5H_5Rh(CNMe)(PMe_3)$ with ArN_3 affords exclusively the carbodiimide complexes $C_5H_5Rh(\kappa^2\text{-}C,N\text{-}MeN{=}C{=}NAr)(PMe_3)$ (**9**, **10**) in good yields. Methylation of **9** and **10** with CF_3SO_3Me, in the presence of NH_4PF_6, gives the cyclic carbene-type derivatives **11** and **12**, of which the first has been characterized by X-ray crystal structure analysis. © 1998 Elsevier Science S.A.

Keywords: Carbodiimide metal complexes; Metallacycles; Aryl azides; Isocyanide metal complexes; Ortho-metallation

1. Introduction

Following earlier work from our laboratory on cycloaddition reactions of isocyanide cobalt compounds $C_5H_5Co(CNR)(PMe_3)$ with 1,2- and 1,3-dipoles [1], we recently found that the same starting materials react with diazoalkanes to yield ketenimine cobalt derivatives [2–4]. This prompted us to study the reactivity of both $C_5H_5Co(CNR)(PMe_3)$ and the analogous rhodium complexes also toward azides RN_3 with the hope that the nitrene fragment :NR, like the carbene unit: CRR′ in the reactions with $R'RCN_2$, would add to the M–CNR bond to form a carbodiimide ligand. While the initial results with $C_5H_5Co(CNCH_2Ph)(PMe_3)$ and $C_5Me_5Co(CNMe)(PMe_3)$ as starting materials seemed to be in complete agreement with our strategy [5], we later discovered that besides the expected carbodiimide cobalt complexes also four-membered metallacycles, built up by the $C_5H_5(PMe_3)Co$ moiety, two isocyanide molecules and a :NAr unit can be formed. The present paper describes the characterization of these metallacycles and reports on the preparation as well as on the unusual ortho-metallation reaction of the half-sandwich-type carbodiimide rhodium derivatives.

2. Results and discussion

The benzylisocyanide cobalt compound **1** reacts with phenylazide in ether to give the corresponding carbodiimide complex $C_5H_5Co(\kappa^2\text{-}C,N\text{-}PhCH_2N{=}C{=}NPh)(PMe_3)$ in moderate yield [5]. In contrast, on treatment of **1** with *p*-tolylazide under the same conditions a mixture of products is formed which contains the carbodiimide derivate **3** (ca. 60%) and the cobaltacycle **5** (ca. 40%) as the main components (Scheme 1). The analogous reaction of the cyclohexylisocyanide complex **2** with phenylazide equally affords a mixture of the carbodiimide compound **4** (ca. 80%) and the corresponding metallacycle **6** (ca. 20%) as the dominating species. Attempts to separate the mixtures of **3**–**5** and **4**–**6** by column chromatography were only partially successful. While the carbodiimide complexes **3** and **4** could not be obtained in analytically pure state (and have therefore been characterized by spectroscopic means), the metallacycles **5** and **6** were isolated as yellow crystalline solids in low yield. The

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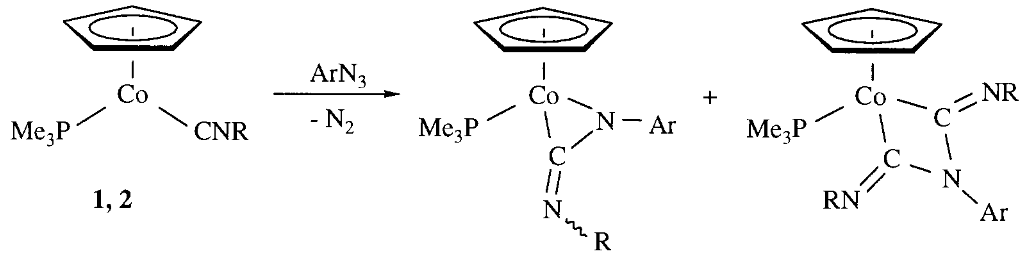
[1] Dedicated to Professor Peter Maitlis on the occasion of his 65th birthday in recognition of his important contributions to organometallic chemistry.



1, 2

3, 4

5, 6

	R
1	CH_2Ph
2	C_6H_{11}

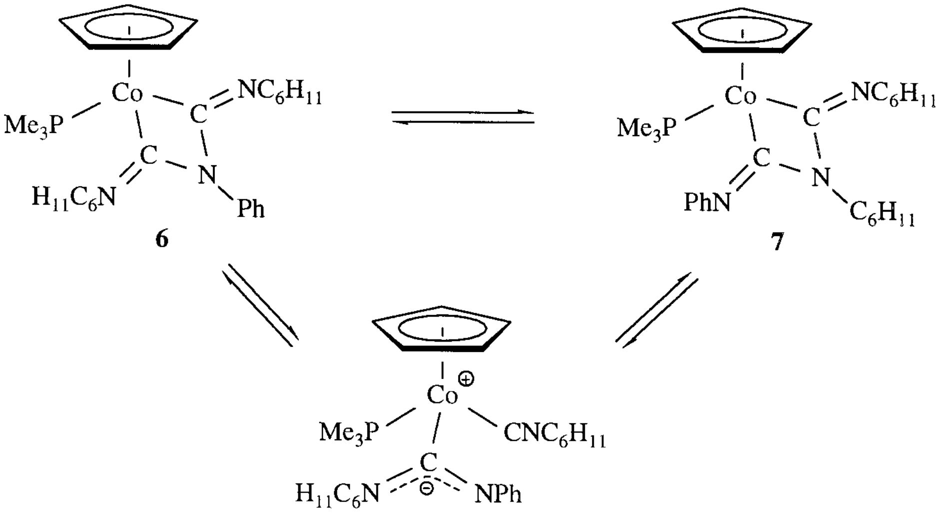
	R	Ar
3, 5	CH_2Ph	p-Tol
4, 6	C_6H_{11}	Ph

Scheme 1.

most typical spectroscopic features of **5** and **6** are the strong C=N stretching frequency at 1605 cm^{-1} in the IR spectra and the doublet at δ 164.0 (for **5**) and 158.6 (for **6**), assigned to the resonance of the CoCN carbon atoms of the metallacycle, in the ^{13}C NMR spectra. The large P–C coupling constant (ca. 30 Hz) of this signal is consistent with the structural proposal. We note that both Hessell and Jones [6] and Riera et al. [7] have already reported the preparation of compounds of the general composition $L_nM[\kappa^2\text{-}C,C\text{-}C(NR)N(R')C(NR)]$ (M = Rh, Fe), the spectroscopic data of which are in good agreement with those of the cobalt complexes **5** and **6**.

With regard to the mechanism of the formation of compounds **5** and **6**, we assume that they result from the insertion of isocyanide (produced by partial decomposition of the starting materials **1** and **2**) into the Co–N bond of the corresponding carbodiimide complex. This has been confirmed by an experiment, carried out in an NMR tube, which illustrated that upon addition of CNC_6H_{11} to a mixture of **4** and **6** in C_6D_6, the amount of the metallacycle increased on the expense of the carbodiimide species.

In benzene solution, compound **6** is somewhat labile and slowly rearranges to the unsymmetrical isomer **7** (see Scheme 2). After 45 days at room temperature, an equilibrium is attained revealing a ratio **6**:**7** of ca. 45:55. Diagnostic for the formation of a four-membered metallacycle with two different NC_6H_{11} units is the ^{13}C NMR spectrum of **7** which displays two distinct signals at δ 63.2 and 54.3 for the NCH carbon atoms and eight resonances at δ ca. 35–25 for the CH_2 carbon atoms of the inequivalent cyclohexyl rings. In order to explain the rearrangement of **6** to **7**, we assume that after breaking one of the N–C bonds of the four-membered ring a zwitterionic intermediate **A** is generated which

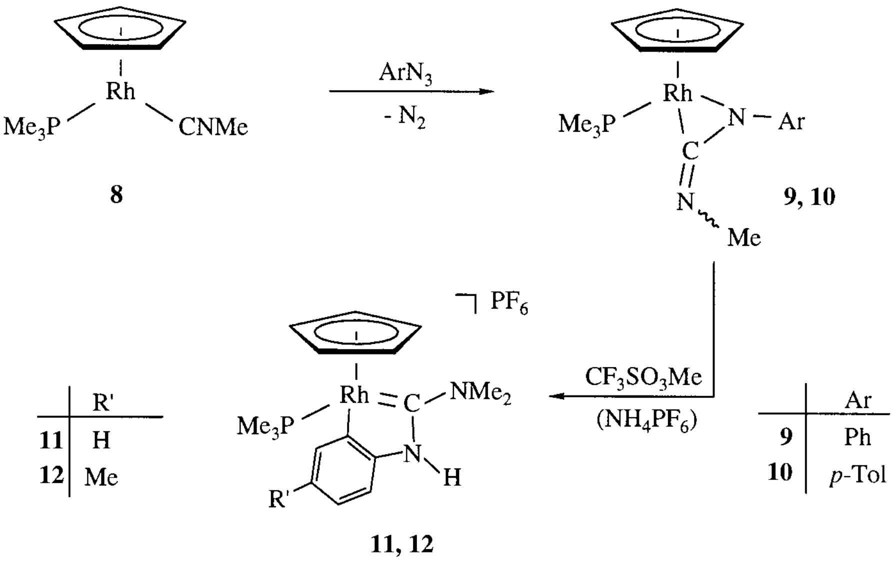


6

7

A

Scheme 2.



Scheme 3.

upon rotation around the Co–C bond forms the thermodynamically somewhat more stable four-membered ring. There is precedence for the conversion of **6** to **7** and vice versa insofar as related cyclopentadienylcobalt derivatives containing a CoC(NMe)SC(NR) metallacycle rearrange thermally to the CoC(S)N(Me)C(NR) isomers [8].

In contrast to the reaction of **1** and **2** with aryl azides, the corresponding reaction of the isocyanide rhodium complex **8** with PhN_3 and p-$MeC_6H_4N_3$ in ether at low

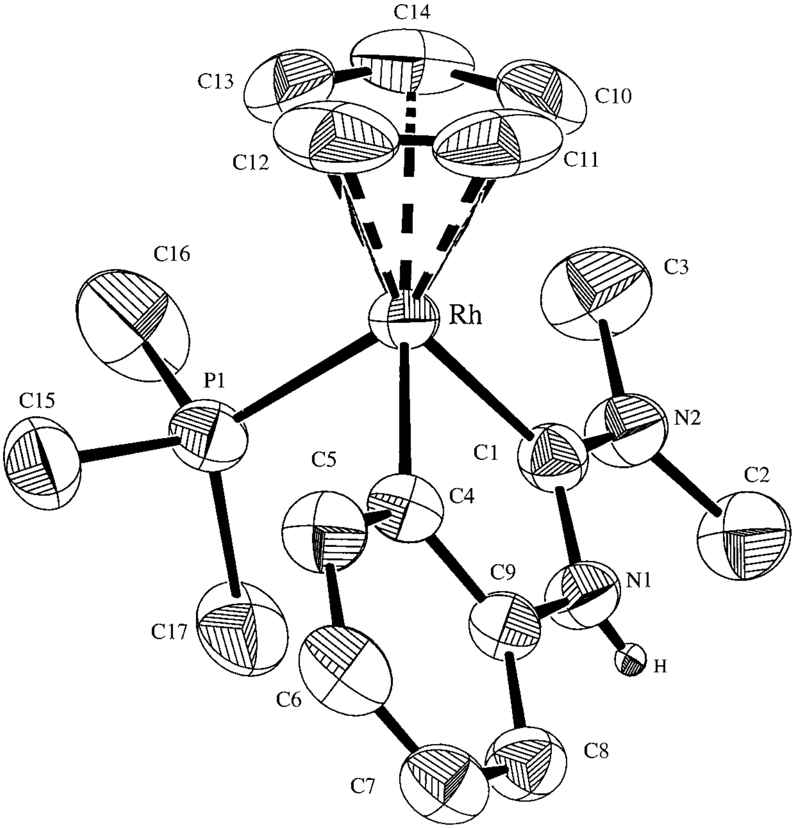


Fig. 1. Molecular structure (ORTEP diagram) of the cation of compound **11**.

temperatures proceeds cleanly and gives the carbodiimide compounds **9** and **10** as red-brown low-melting solids in 60–70% yield (Scheme 3). Similar to the IR spectra of **3** and **4**, those of **9** and **10** also display a strong N=C=N stretching frequency at 1720–1740 cm^{-1} which is indicative for the dihapto coordination of the carbodiimide unit. This absorption is significantly shifted to a lower energy relative to both that of the free carbodiimide (2120–2140 cm^{-1}) and that expected for an N-bonded ligand [9]. Further evidence for the coordination of a C,N-bonded moiety comes from the ^{13}C NMR spectra which possess a doublet of doublets at δ 156.2 (for **9**) and 156.9 (for **10**) assigned to the central carbon atom of the MeN=C=NAr unit. In particular, the large Rh–C coupling constant of ca. 17.5 Hz suggests that the carbodiimide is bonded via N and C to the rhodium. The ^{13}C NMR spectra of the cobalt compounds **3** and **4** (see Scheme 1) also display a resonance (doublet due to P–C coupling) at δ 162.7 (**3**) and 157.7 (**4**), respectively, thus supporting the structural proposal.

The methylation of **9** and **10** takes an unexpected course. While the analogous cobalt complex $C_5Me_5Co(\kappa^2\text{-}C,N\text{-}MeN{=}C{=}NAr)(PMe_3)$ react with methyliodide to give the cationic species $[C_5Me_5Co(\kappa^2\text{-}C,N\text{-}Me_2N{=}C{=}NAr)(PMe_3)]^+$, still containing a CoCN three-membered ring, on treatment of **9** and **10** with methyltriflate, in the presence of NH_4PF_6, the orthometallated compounds **11** and **12** are formed. The ionic structure shown in Scheme 3 has been confirmed by conductivity measurements which are consistent with the presence of 1:1 electrolytes. In the IR spectra of **11** and **12** the N=C=N stretch is shifted by 160–180 cm^{-1} to lower wave numbers compared with the precursors **9** and **10**, which indicates that in the methylated products the C=NR double bond character is significantly reduced. Since in the ^1H NMR spectra of **11** and **12**, two signals for the $N(CH_3)_2$ protons (of which only one is split into a doublet) of equal intensity are observed, we conclude that like in other aminocarbene complexes [10] the rotation around the $C{-}NMe_2$ bond is strictly hindered. In the ^{13}C NMR spectra of **11** and **12**, the resonance for the carbene-type carbon atom appears at δ 202.5 (for **11**) and 202.1 (for **12**) and that of the metal-bonded C atom of the aryl ring at δ 142.4 (for **11** and **12**). Both signals show strong Rh–C and P–C couplings. The presence of a NH moiety in the five-membered RhCCNC ring of **11** and **12** is shown by a broadend signal at $\delta \sim 8.4$ in the ^1H NMR and a corresponding absorption at 3370–3375 cm^{-1} in the IR spectra.

In order to confirm the proposed structure for the orthometallated compounds, an X-ray crystal structure analysis of **11** was carried out. The ORTEP drawing (Fig. 1) reveals that the rhodium is coordinated in a pseudo-octahedral fashion with the cyclopentadienyl ligand occupying three coordination sites. The metallacycle Rh–C1–N1–C9–C4 is almost perfectly planar and the carbon atoms C5–C8 of the annelated ring are located in the same plane. The dihedral angle between the five- and the six-membered rings is 1.2°. In agreement with the carbene-like structure, the distance Rh–C1 is somewhat shorter than Rh–C4 and lies in the range of Rh–C bond lengths found in other half-sandwich-type carbene rhodium complexes [11–15]. A partial π-bond contribution is also indicated in the C1–N1 and C1–N2 distances (Table 1) which are expectedly longer than that of a C=N double bond [16] but significantly shorter than the N2–C2 and N2–C3 bonds. The distances between the metal and the cyclopentadienyl carbon atoms differ slightly but overall agree with those of other C_5H_5Rh complexes with a piano-stool configuration [17–27]. Finally, we note that a cationic cobalt compound with the same structure as that of **11** is known but has been prepared on a completely different route [28].

Table 1
Selected bond distances (Å) and bond angles (deg) of **11** (with e.s.d.s in parentheses)

Bond distances (Å)		Bond angles (deg)	
Rh–C1	1.977(3)	C1–Rh–C4	78.6(1)
Rh–C4	2.028(3)	C1–Rh–P1	91.3(1)
Rh–P1	2.236(1)	C4–Rh–P1	85.7(1)
Rh–C10	2.243(4)	C1–N1–C9	117.5(3)
Rh–C11	2.184(4)	C1–N2–C2	121.3(3)
Rh–C12	2.160(4)	C1–N2–C3	122.9(3)
Rh–C13	2.220(4)	C2–N2–C3	115.8(3)
Rh–C14	2.272(4)	N1–C1–N2	117.1(3)
N1–C1	1.345(4)	Rh–C1–N2	127.5(3)
N1–C9	1.373(4)	Rh–C1–N1	115.4(2)
N2–C1	1.301(4)	Rh–C4–C9	115.0(2)
N2–C2	1.445(5)	Rh–C4–C5	129.0(3)
N2–C3	1.454(5)	N1–C9–C4	113.4(3)

3. Experimental section

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1** [5], **2** [3] and **8** [29] were prepared by published methods. IR: Perkin-Elmer 1420; NMR: Jeol FX 90 Q and Bruker AMX 400. Equivalent conductivity Λ was measured in CH_3NO_2. Melting and decomposition points were determined by DTA.

3.1. Reaction of $C_5H_5Co(CNCH_2Ph)(PMe_3)$ (1) with $p\text{-}MeC_6H_4N_3$

A solution of 295 mg (0.93 mmol) of **1** in 20 ml of ether was treated at −78°C with 0.53 ml of a 1.74 M solution (0.93 mmol) of *p*-tolylazide in ether. A rapid change of color from orange-red to dark green, accompanied by the evolution of gas (N_2), occurred. After the solution was warmed to room temperature, the solvent was removed in vacuo. The oily residue was dissolved in 4 ml of ether and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, 5 cm column). With ether, a green fraction was eluted which was brought to dryness in vacuo. Due to the ^1H NMR spectrum, the oily green residue consisted (besides some impurities) of ca. 60% of **3** and ca. 40% of **5**. The mixture of products was then extracted with 15 ml of pentane and the residue recrystallized from ether–pentane 1:3. Upon storing the solution at −78°C for 12 h, a yellow crystalline solid **5** was obtained. Yield 20 mg (4%); dec. temp. 151°C. The pentane extract contained mainly compound **3**, which could not be separated from small amounts of byproducts and was therefore characterized by spectroscopic techniques.

3: IR (C_6H_6): ν(N=C=N) 1710 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 8.06–6.94 (m; 9H; C_6H_5 and C_6H_4), 5.41 (s; 2H; NCH_2), 4.45 (d; J(PH) = 0.5 Hz; 5H; C_5H_5), 2.14 (s; 3H; $C_6H_4CH_3$), 0.63 (d; J(PH) = 10.4 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 162.7 (d; J(PC) = 13.7 Hz; CoCN), 147.6, 143.9 (both s; *ipso*-C of C_6H_5 and C_6H_4), 129.9, 129.5, 128.3, 127.8, 126.4, 125.1, 121.9 (all s; C_6H_5 and C_6H_4), 128.6 (d; J(PC) = 1.7 Hz; C_6H_5 or C_6H_4), 82.2 (d; J(PC) = 1.9 Hz; C_5H_5), 60.1 (d; J(PC) = 2.8 Hz; NCH_2), 21.1 (s; $C_6H_4CH_3$), 17.7 (d; J(PC) = 27.6 Hz; PCH_3).

5: Anal. Found: C, 68.82; H, 6.38; N, 7.76. $C_{31}H_{35}CoN_3P$ calcd.: C, 69.01; H, 6.54; N, 7.79. IR (C_6H_6): ν(C=N) 1605 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 9.12–7.05 (m; 14H; C_6H_5 and C_6H_4), 4.68 (s; 4H; NCH_2), 4.58 (d; J(PH) = 0.4 Hz; 5H; C_5H_5), 2.10 (s; 3H; $C_6H_4CH_3$), 0.80 (d; J(PH) = 9.8 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 164.0 (d; J(PC) = 29.8 Hz; CoCN), 143.6 (s; *ipso*-C of C_6H_4), 138.2 (d; J(PC) = 4.2 Hz; *ipso*-C of C_6H_5), 132.0, 129.7, 128.7, 128.6, 128.1, 127.9, 127.3, 126.4, 123.6, 119.8 (all s; C_6H_5 and C_6H_4), 84.5 (d; J(PC) = 1.9 Hz; C_5H_5), 59.4 (d; J(PC) = 1.2 Hz; NCH_2), 21.0 (s; $C_6H_4CH_3$), 19.7 (d; J(PC) = 30.5 Hz; PCH_3).

3.2. Reaction of $C_5H_5Co(CNC_6H_{11})(PMe_3)$ (2) with PhN_3

This reaction was performed analogously as described in Section 3.1. using 552 mg (1.78 mmol) of **2** and 195 μl. (1.78 mmol) of phenylazide as starting materials. The mixture of products, which was obtained after column chromatography on Al_2O_3, consisted (besides some impurities) of ca. 80% of **4** and ca. 20% of **6**. The subsequent work-up procedure gave **6** as a yellow crystalline solid. Yield 30 mg (3%); dec. temp. 140°C. Compound **4** could not be separated from some byproducts and was characterized by spectroscopic techniques.

4: ^1H NMR (90 MHz, C_6D_6): δ 9.07–6.37 (m; 5H; C_6H_5), 4.48 (s; 5H; C_5H_5), 4.05 (m; 1H; NCH), 2.32–0.35 (m; 10H; CH_2 of C_6H_{11}), 0.70 (d; J(PH) = 9.7 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 157.7 (d; J(PC) = 13.3 Hz; CoCN), 150.9 (s; *ipso*-C of C_6H_5), 129.7, 129.1, 128.1, 122.0, 119.3 (all s; C_6H_5), 82.1 (s; C_5H_5), 64.9 (d; J(PC) = 2.7 Hz; NCH), 37.2, 36.1, 26.7, 25.8, 25.7 (all s; CH_2 of C_6H_{11}), 17.8 (d; J(PC) = 27.5 Hz; PCH_3).

6: Anal. Found: C, 65.94; H, 8.37; N, 8.18. $C_{28}H_{41}CoN_3P$ calcd.: C, 66.00; H, 8.11; N, 8.25. IR (C_6H_6): ν(C=N) 1605 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 9.13–6.35 (m, 5H; C_6H_5), 4.69 (d, J(PH) = 0.4 Hz; 5H; C_5H_5), 2.92 (m; 2H; NCH), 1.82–0.86 (m, 20H; CH_2 of C_6H_{11}), 0.95 (d; J(PH) = 9.9 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 158.6 (d, J(PC) = 30.0 Hz; CoCN), 140.6 (d; J(PC) = 4.1 Hz; *ipso*-C of C_6H_5), 128.6, 127.9, 127.8, 123.8, 122.5 (all s; C_6H_5), 84.4 (d; J(PC) = 2.0 Hz; C_5H_5), 63.6 (s, br; NCH), 36.3, 36.2, 26.6, 25.5, 25.4 (all s; CH_2 of C_6H_{11}), 19.8 (d; J(PC) = 30.2 Hz; PCH_3).

3.3. Partial rearrangement of 6 to 7

A solution of 20 mg (0.04 mmol) of **6** in 2 ml of C_6D_6 was stored in an NMR tube at room temperature. After 14 d, a ratio of **6**:**7** = 60:40 was determined. After 45 d, the ratio **6**:**7** had been changed to 45:55. The isomer **7** was characterized by spectroscopic techniques. IR (C_6H_6): ν(C=N) 1575 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 9.14–6.75 (m; C_6H_5), 4.55 (d; J(PH) = 0.4 Hz; C_5H_5), 2.77 (m; NCH), 2.22–0.67 (m; CH_2 of C_6H_{11}), 1.03 (d; J(PH) 9.9 Hz; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 158.6 (d; J(PC) = 30.0 Hz; CoCN), 153.7 (s; *ipso*-C of C_6H_5), 129.1, 128.5, 128.1, 123.2, 121.3 (all s; C_6H_5), 84.1 (d; J(PC) = 2.0 Hz; C_5H_5), 63.2, 54.3 (both s; NCH), 36.5, 36.3, 30.8, 26.8, 26.7, 26.6, 26.1, 25.7 (all s; CH_2 of C_6H_{11}), 20.0 (d; J(PC) = 30.1 Hz; PCH_3).

3.4. Preparation of $C_5H_5Rh(\kappa^2\text{-}C,N\text{-}MeN{=}C{=}NPh)(PMe_3)$ (9)

A solution of 301 mg (1.06 mmol) of **8** in 15 ml of ether was treated at −78°C with 115 μl (1.06 mmol) of phenylazide. A change of color from orange-yellow to red-brown, accompanied by the evolution of gas (N_2), occurred. The solution was warmed to room temperature, and the solvent was removed in vacuo. The oily residue was extracted with 25 ml of pentane, the extract was filtered, and the filtrate was concentrated to ca. 10 ml in vacuo. After the solution was stored at −78°C, red-brown crystals precipitated which became an oil upon warming to ca. 10°C. Yield 255 mg (64%). Anal. Found: C, 50.41; H, 5.43; N, 7.40. $C_{16}H_{22}N_2PRh$ calcd.: C, 51.08; H, 5.89; N, 7.45. IR (C_6H_6): ν(N=C=N) 1740, 1720 cm^{-1}. ^1H NMR (90 MHz,

C_6D_6): δ 7.78–6.68 (m; 5H; C_6H_5), 4.85 (dd; J(PH) = 1.1, J(RhH) = 0.7 Hz; 5H; C_5H_5), 3.42 (d; J(RhH) = 0.3 Hz; 3H; NCH_3), 0.82 (dd; J(PH) = 10.4, J(RhH) = 1.1 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 156.2 (dd; J(RhC) = 17.4, J(PC) = 7.2 Hz; RhCN), 152.3 (s; *ipso*-C of C_6H_5), 128.6, 121.5, 120.0 (all s; C_6H_5), 85.7 (dd; J(PC) = J(RhC) = 3.4 Hz; C_5H_5), 43.3 (s; NCH_3), 19.4 (dd; J(PC) = 30.6, J(RhC) = 1.2 Hz; PCH_3). ^{31}P NMR (36.2 MHz, C_6D_6): δ 8.0 (d; J(RhP) = 186.1 Hz).

3.5. Preparation of $C_5H_5Rh(\kappa^2\text{-}C,N\text{-}MeN{=}C{=}NC_6H_4\text{-}p\text{-}CH_3)(PMe_3)$ (**10**)

Compound **10** was prepared as described for **9**, using 172 mg (0.60 mmol) of **8** and 347 μl of a 1.74 M solution (0.60 mmol) of *p*-tolylazide in ether as starting materials. A red-brown solid, which melts above ca. 15°C, was isolated. Yield 146 mg (62%). Anal. Found: C, 52.25; H, 6.40; N, 7.57. $C_{17}H_{24}N_2PRh$ calcd.: C, 52.32; H, 6.20, N, 7.18. IR (C_6H_6): ν(N=C=N) 1725 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 7.77–6.96 (m; 4H; C_6H_4), 4.91 (dd; J(PH) = 1.1, (RhH) = 0.7 Hz; 5H; C_5H_5), 3.48 (d; J(RhH) = 0.4 Hz; 3H; NCH_3), 2.13 (s; 3H; $C_6H_4CH_3$), 0.86 (dd; J(PH) = 10.4, J(RhH) = 1.1 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 156.9 (dd; J(RhC) = 17.5, J(PC) = 7.2 Hz; RhCN), 149.9 (s; *ipso*-C of C_6H_5), 129.3, 128.9, 121.4 (all s; C_6H_5), 85.8 (dd; J(PC) = J(RhC) = 3.3 Hz; C_5H_5), 43.4 (s; NCH_3), 20.9 (s; $C_6H_4CH_3$), 19.5 (dd; J(PC) = 29.9, J(RhC) = 1.1 Hz, PCH_3). ^{31}P NMR (36.2 MHz, C_6D_6): δ 8.0 (d; J(RhP) = 187.6 Hz).

3.6. Preparation of $[C_5H_5Rh(\kappa^2\text{-}C,C\text{-}C(NMe_2)NHC_6H_4)(PMe_3)]PF_6$ (**11**)

A solution of 95 mg (0.25 mmol) of **9** in 5 ml of ether was treated at −78°C with 35 μl (0.31 mmol) of methyltriflate. A brown oily precipitate was formed which was separated from the almost colorless mother liquor. After the residue was washed twice with 5 ml portions of ether, it was stirred with a solution of 45 mg (0.28 mmol) of NH_4PF_6 in 3 ml of methanol. A light-brown solid precipitated which was filtered, washed twice with 2 ml portions of methanol and dried in vacuo. The solid was dissolved in 3 ml of methanol–acetone (1:5), the solution was layered with 20 ml of ether and stored at 0°C. After 12 h, yellow-brown crystals were obtained. Yield 100 mg (74%); dec. temp. 286°C. Anal. Found: C, 38.01; H, 4.68; N, 5.18. $C_{17}H_{25}F_6N_2P_2Rh$ calcd.: C, 38.08; H, 4.70; N, 5.22. Λ 85 cm^2 Ω^{-1} mol^{-1}. IR (C_6H_6): ν(NH) 3375, ν(C=N) 1550, ν(PF) 840 cm^{-1}. ^{1}H NMR (90 MHz, CD_3NO_2): δ 8.44 (s, br; 1H; NH), 7.52–6.69 (m; 4H; C_6H_4), 5.64 (dd; J(PH) = 1.2, J(RhH) = 0.4 Hz; 5H; C_5H_5), 3.64 (s; 3H; NCH_3), 3.34 (d; J(PH) = 1.0 Hz; 3H; NCH_3), 1.38 (dd; J(PH) = 11.4, J(RhH) = 1.0 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 202.5 (dd; J(RhC) = 49.8, J(PC) = 19.2 Hz; RhCN), 152.0 (s; C(2) of C_6H_4), 142.4 (dd; J(RhC) = 32.7, J(PC) = 17.3 Hz; *ipso*-C of C_6H_4), 141.6, 125.7, 122.9, 113.3 (all s; C_6H_4), 93.2 (dd; J(PC) = J(RhC) = 2.6 Hz; C_5H_5), 50.3, 38.4 (both s; NCH_3), 18.6 (dd; J(PC) = 36.2, J(RhC) = 1.3 Hz; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 10.2 (d; J(RhP) = 135.0 Hz; PMe_3), −144.4 (sept; J(PF) = 707.2 Hz; PF_6).

3.7. Preparation of $[C_5H_5Rh(\kappa^2\text{-}C,C\text{-}C(NMe_2)NHC_6H_3Me)(PMe_3)]PF_6$ (**12**)

Compound **12** was prepared as described for **11**, using 80 mg (0.20 mmol) of **10**, 30 μl (0.27 mmol) of methyltriflate and 34 mg (0.21 mmol) of NH_4PF_6 as starting materials. A yellow-brown solid was isolated. Yield 81 mg (72%), dec. temp. 247°C. Anal. Found: C, 39.50; H, 4.88; N, 5.05. $C_{18}H_{27}F_6N_2P_2Rh$ calcd.: C, 39.29; H, 4.95; N, 5.09. Λ 79 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(NH) 3370, ν(C=N) 1560, ν(PF) 840 cm^{-1}. ^{1}H NMR (90 MHz, CD_3NO_2): δ 8.37 (s, br; 1H; NH), 7.34 (s, br; 1H; one H of C_6H_3), 6.85 (m; 2H; two H of C_6H_3), 5.62 (dd; J(PH) = 1.2, J(RhH) = 0.4 Hz; 5H, C_5H_5), 3.62 (s; 3H; NCH_3), 3.31 (d; J(PH) = 1.0 Hz; 3H; NCH_3), 2.26 (s; 3H; $C_6H_3CH_3$), 1.37 (dd; J(PH) = 11.4, J(RhH) = 1.0 Hz; 9H; PMe_3). ^{13}C NMR (100.6 MHz, CD_3NO_2): δ 202.1 (dd; J(RhC) = 49.4, J(PC) = 19.1 Hz; RhCN), 149.6 (s; C(2) of C_6H_3), 142.4 (dd; J(RhC) = 32.6, J(PC) = 17.3 Hz; *ipso*-C of C_6H_3), 142.2 (d; J(PC) = 3.0 Hz, one C of C_6H_3), 132.5 (s; C(5) of C_6H_3), 93.1 (dd; J(PC) = J(RhC) = 2.4 Hz; C_5H_5), 50.2, 38.3 (both s; NCH_3), 21.1 (s; $C_6H_3CH_3$), 18.6 (d; J(PC) = 36.6 Hz; PCH_3). ^{31}P NMR (36.2 MHz, CD_3NO_2): δ 10.2 (d; J(RhP) = 135.0 Hz; PMe_3), −144.4 (sept; J(PF) = 707.2 Hz; PF_6).

3.8. Crystal structure analysis of **11**

Single crystals were grown by slow diffusion of ether into a solution of **11** in methanol–acetone (1:5). Crystal data (from 25 reflections with $11° < \Theta < 14°$): monoclinic, space group $P2_1/c$ (no. 14), $a = 8.196(1)$ Å, $b = 15.212(3)$ Å, $c = 16.729(3)$ Å, $\beta = 100.39(1)°$, $V = 2051.5(6)$ Å^3, $Z = 4$, $d_{calcd} = 1.736$ g cm^{-3}, $\mu = 1.037$ mm^{-1}. Crystal size 0.2 × 0.3 × 0.4 mm^3. Enraf Nonius CAD4 diffractometer, Mo Kα radiation (0.70930 Å), graphite monochromator, $T = 293$ K, ω/Θ scan, max. $2\Theta = 48°$; 3569 reflections measured, 3315 reflections independent, 3023 regarded as being observed [$I > 2\sigma(I)$]; intensity data corrected for Lorentz and polarization effects, empirical absorption correction applied, minimum transmission 95.44%. The structure was solved by direct methods; atomic coordinates were refined by full-matrix least squares (278 parameters, unit weights, Enraf Nonius SDP). The position of the hydrogen atom at N1 was taken from a difference Fourier synthesis and refined by using the riding model. The positions of the other hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å). $R = 0.0282$, $R_w = 0.036$; reflex:parameter ratio 11.16; residual electron density $+1.206/-0.294$ e Å^{-3}. Detailed crystallographic data (excluding structure factors) for the structure of **11** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC100848. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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