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Reactions of (Isocyanide)cobalt Complexes with Azides: A Template Synthesis of Carbodiimides on a Transition-Metal Center

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The (isocyanide)cobalt compounds [$C_5H_5Co(CNCH_2Ph)(PMe_3)$] (**2**) and [$C_5Me_5Co(CNMe)(PMe_3)$] (**5**), which are prepared from the bis(phosphine) derivatives [$C_5H_5Co(PMe_3)_2$] or [$C_5Me_5Co(PMe_3)_2$] and isocyanide, react with phenyl or 4-tolyl azide RN_3 to give the η^2-carbodiimide complexes [$C_5H_5Co(\eta^2(C,N(Ph))$-$PhCH_2N{=}C{=}NPh)(PMe_3)$] (**3**) and [$C_5Me_5Co(\eta^2(C,N(R))$-$MeN{=}C{=}NR)(PMe_3)$] (**6**, **7**), respectively. The reaction is regiospecific with respect to coordination of the unsymmetrical carbodiimide ligand. Treatment of **6** and **7** with methyl iodide produces, after reprecipitation with NH_4PF_6, the ionic complexes [$C_5Me_5Co(\eta^2(C,N(R))$-$Me_2N{=}C{=}NR)(PMe_3)$]PF_6 (**8**, **9**) in 80% yield. Compound **8** (R = Ph) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 8.786(1) Å, b = 9.067(1) Å, c = 17.938(3) Å, α = 79.73(1)°, β = 75.82 (1)°, γ = 77.56(1)°, V = 1341.2 Å^3, and Z = 2. The structure of **8** confirms the bidentate bonding of the amidinyl ligand in which the positive charge is partially delocalized. The complexes **3** and **6** react with iodine in ether/benzene to give the free carbodiimide together with [$C_5R_5Co(PMe_3)I_2$] (R = H, Me).

Introduction

The recent discovery that (isocyanide)cobalt compounds of the general composition [$C_5H_5Co(CNR)(PMe_3)$] react not only with 1,2- or 1,3-dipoles to give four- or five-membered metallaheterocycles[1,2] but also with diazoalkanes to produce ketenimine cobalt complexes[3] prompted us to study the reactivity of the same half-sandwich type compounds toward azides. Most recently, Hessell and Jones have shown[4] that on treatment of the bis(isocyanide)rhodium derivatives [$Tp'Rh(CNR)_2$] and [$C_5Me_5Rh(CNR)_2$] (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate) with phenyl or 2,4-xylyl azide the corresponding carbodiimide complexes are formed. Although no intermediates could be observed, the authors assumed that the first step in the reaction is a 1,3-dipolar cycloaddition of the azide to the Rh=CNR bond which is followed by the expulsion of nitrogen from the highly labile, five-membered ring system.[4] A similar mechanism has been proposed by us for the addition of tosyl and 2-nitrophenyl azide to the rhodium—carbon double bond of the vinylidene complexes [$C_5H_5Rh({=}C{=}CHR)(P\textit{i}Pr_3)$] which leads to the formation of both *N*,*C*- and *C*,*C*-bonded ketenimine rhodium derivatives.[5]

Here we report the synthesis of (carbodiimide)cobalt complexes in which the metal is linked either to a cyclopentadienyl or a pentamethylcyclopentadienyl ring. These are, to our knowledge, the first stable (carbodiimide)cobalt complexes in which the heterocumulene $RN{=}C{=}NR'$ is coordinated to cobalt as a *dihapto*-bonded ligand. We note that, from the heavier elements in the cobalt triad, compounds of the general type [$L_nM(\eta^2$-$RN{=}C{=}NR')$] are already known. In addition to Jones's work,[4] van Gaal and Verlaan[6] prepared the square-planar rhodium(I) complex *trans*-[$RhCl(\eta^2$-$RN{=}C{=}NR)(PCy_3)_2$] (R = 4-tolyl) whereas Bergman et al.[7] reported the synthesis of [$C_5Me_5Ir(\eta^2$-$RN{=}C{=}NR)(CNR)$] (R = *t*Bu); the latter is formed by addition of two molecules of CN*t*Bu to the iridium nitrene complex [$C_5Me_5Ir({\equiv}N\textit{t}Bu)$]. We also report the methylation of the compounds [$C_5Me_5Co(\eta^2$-$RN{=}C{=}NR')(PMe_3)$] to give cationic amidinylmetal derivatives and the expulsion of the carbodiimide ligands from the cobalt complexes under mild conditions on treatment with iodine.

Results

Preparation and Reactivity of Carbodiimide Complexes 3, 6, and 7. Following earlier work from our laboratory on the synthesis of the carbonyl compounds [$C_5H_5Co(CO)(PMe_3)$][8] and [$C_5Me_5Co(CO)(PMe_3)$][9], the reaction of [$C_5H_5Co(PMe_3)_2$] (**1**) and [$C_5Me_5Co(PMe_3)_2$] (**4**) with benzyl or methyl isocyanide gives the (isocyanide)(trimethylphosphine)cobalt complexes **2** and **5** in almost quantitative yield (Scheme I). Both compounds are orange-red low-melting substances which are extremely air-sensitive and soluble in all common organic solvents. The C≡N stretching frequency of **2** and **5** appears at relatively low wavenumbers which is in agreement with the presence of an electron-rich metal center.

Addition of phenyl azide to an ether solution of **2** at −78 °C results in the immediate evolution of nitrogen gas and

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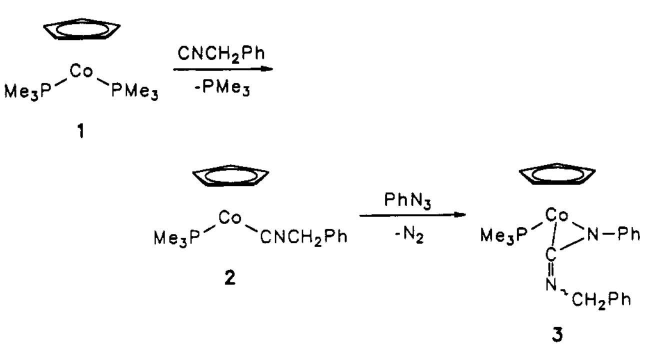
Scheme I



a characteristic change of color from orange-red to green. Warming of the solution to room temperature and removal of the solvent gives, after extraction and recrystallization from ether, green crystals which analyze as [$C_5H_5Co(\eta^2$-$PhCH_2N{=}C{=}NPh)(PMe_3)$] (**3**). Attempts to obtain analogous carbodiimide complexes from [$C_5H_5Co(CNR)(PMe_3)$] (R = Me, *t*Bu)[10] and phenyl azide failed.

The pentamethylcyclopentadienyl compounds **6** and **7** were prepared from **5** and phenyl or 4-tolyl azide in 60% yield. In contrast to **3**, they are red-brown solids which are much less air-sensitive than the (isocyanide)cobalt precursors. Both **3** as well as **6** and **7** have been fully characterized by elemental analysis and IR and ^1H and ^{13}C NMR spectroscopy. The dihapto coordination of the carbodiimide ligand is already indicated by the IR spectra which display a strong N=C=N stretching frequency at ca. 1700 cm^{-1}. 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 a N-bonded ligand.[11] It should be mentioned that the decrease in frequency of more than 400 cm^{-1} is of a magnitude similar to that observed for the Tp′Rh and C_5Me_5Rh carbodiimide complexes.[4]

Further evidence for the presence of a η^2-RN=C=NR′ unit in **3**, **6** and **7** comes from the $^{13}C\{^1H\}$ NMR spectra which possess a doublet at ca. δ 161 assigned to the central carbon of the heterocumulene ligand. The PC coupling constant of 14–15 Hz strongly suggests that the carbon of the carbodiimide is directly bonded to the metal. We note that in the $^{13}C\{^1H\}$ NMR spectrum of the related phenyl isocyanate derivative [$C_5Me_5Co(\eta^2$-*C,N*-$PhN{=}C{=}O)(PMe_3)$] the signal of the isocyanate carbon is observed at δ 170.6 with a $^2J(^{31}P, ^{13}C)$ of 19 Hz.[12]

If the C_5Me_5Co complexes **6** and **7** react with methyl iodide, the attack of the electrophile is directed to the exocyclic =NR group. Treatment of **6** or **7** in ether at room temperature with a 2-fold excess of CH_3I leads to the formation of a crude reaction product which, after addition of NH_4PF_6 and reprecipitation, gives green, moderately air-sensitive crystals which analyze as [$C_5Me_5Co(\eta^2$-$Me_2N{=}C{=}NPh)(PMe_3)$]PF_6 (**8**) and [$C_5Me_5Co(\eta^2$-$Me_2N{=}C{=}NTol)(PMe_3)$]PF_6 (**9**), respectively. The ionic structure (Scheme II) is shown by conductivity measurements (in CH_3NO_2) which are consistent with the presence of 1:1 electrolytes. As in the IR spectra of **8** and **9** the N=C=N stretching frequency is only shifted by 10–25 cm^{-1} to lower wavenumbers compared with the (carbodiimide)metal precursors, we conclude that despite the addition of the metal cation the coordination mode of the N=C=N unit is only slightly changed. The ^1H NMR spectra of **8** and **9** show two signals for the $N(CH_3)_2$ protons of equal intensity which we assign to the exo and endo position of the methyl groups and thus indicate a strictly hindered rotation around the C—NMe_2 bond. In the ^{13}C NMR spectra of **8** and **9**, the resonance of the cobalt-bound carbon of the CoCN three-membered ring appears at δ 171–172 and is split due to PC coupling into a doublet. The shift by ca. 10 ppm to lower field compared with **6** and **7** is attributed to a somewhat reduced electron density at the N=C=N carbon and is consistent with the positive charge of the complexes.

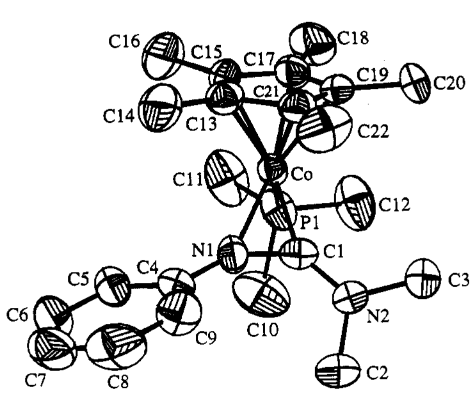
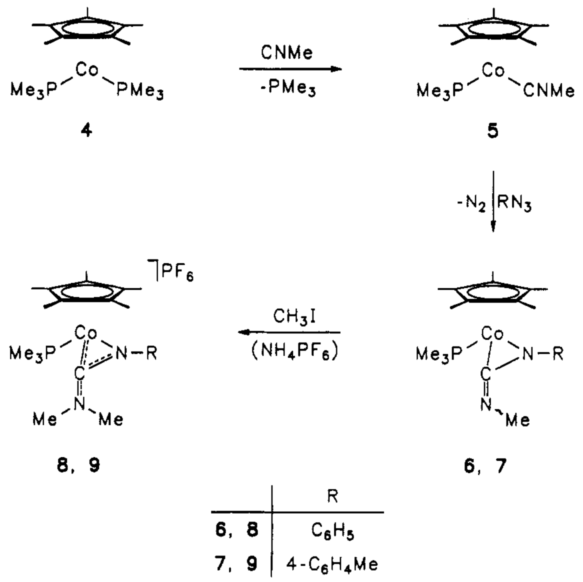


Figure 1. ORTEP drawing of complex **8**.

Scheme II



	R
6, 8	C_6H_5
7, 9	4-C_6H_4Me

Molecular Structure of 8. A single-crystal X-ray structure analysis of compound **8** confirms the structural proposal shown in Scheme II. The ORTEP drawing (Figure 1) reveals that the amidinyl ligand is bonded via carbon and nitrogen to cobalt and that the bending of the C4, N1, C1, N2 unit [with bond angles C4–N1–C1 = 139.3(5)° and N1–C1–N2 = 136.5(5)°] is very similar to that found in alkyne–metal complexes.[13] The nitrogen atom N2 and the atoms Co, C1, and N1 of the three-membered ring lie in the same plane which is only slightly twisted (by ca. 6°) to the plane N2, C1, C2, C3.

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Table I. Selected Bond Distances and Angles with Esd's for 8

	Bond Distances (Å)		
Co–P1	2.197(2)	Co–C21	2.080(5)
Co–N1	1.953(4)	N1–C1	1.267(7)
Co–C1	1.854(6)	N1–C4	1.389(7)
Co–C13	2.090(6)	N2–C1	1.328(7)
Co–C15	2.089(6)	N2–C2	1.467(7)
Co–C17	2.076(6)	N2–C3	1.455(7)
Co–C19	2.081(5)		
	Bond Angles (deg)		
P1–Co–N1	93.0(2)	C1–N2–C2	122.8(5)
P1–Co–C1	91.2(2)	C1–N2–C3	121.0(5)
N1–Co–C1	38.8(2)	C2–N2–C3	115.7(5)
Co–N1–C1	66.4(3)	Co–C1–N1	74.8(3)
Co–N1–C4	145.0(4)	Co–C1–N2	148.6(5)
C1–N1–C4	139.3(5)	N1–C1–N2	136.5(5)

The Co—C1 distance (1.854(6) Å) is significantly shorter than that expected for a Co—C single bond (cf. Co—CH_3 in $[(C_5H_4CF_3)CoCH_3(PMe_3)_2]^+$: 2.014(6) Å)[14] and comparable to that found in the related ketenimine cobalt derivative $[C_5H_5Co(\eta^2\text{-}C,C\text{-}RN{=}C{=}C(4\text{-}C_6H_4Cl)_2)(PMe_3)]$ (R = (*S*)-CH(Ph)CH_3).[3b] A partial π-bond contribution is not only indicated in the Co—C1 but also in the C1—N2 distance (1.328(7) Å) which is slightly longer than the N1—C1 distance (1.267(7) Å); it is however much shorter than the N2—C2 and N2—C3 bond lengths (1.467(7) and 1.455 (7) Å). The N1—C1 distance exactly corresponds to that for a C=N double bond[15] and is almost identical to that found in the MCN three-membered ring of $[C_5H_5Co(\eta^2\text{-}C,N\text{-}CyN{=}C{=}C(C_{12}H_8))(PMe_3)]$ (Cy = C_6H_{11}),[3b] $[Tp'Rh(\eta^2\text{-}C,N\text{-}RN{=}C{=}NR')(CNR')]$ (R = 2,4-xylyl, R' = 2-tolyl),[4] and $[(C_5H_5)_2V(\eta^2\text{-}C,N\text{-}R(CH_3)N{=}C{=}NR)]I_3$ (R = 4-tolyl).[16]

Finally, it is interesting to note that whereas the C_5 ring of the pentamethylcyclopentadienyl ligand is planar, the carbon atoms C16, C20, and in particular C18 of the methyl substituents stick out of the ring and point away from the metal. That the bending is more distinct for C16, C18, and C20 than for C14 and C22 is possibly due to some steric hindrance between the CH_3 groups of the cyclopentadienyl and the phosphine ligand. The distances between the metal and the C_5 ring carbons differ only slightly which could be seen as an indication of a similar degree of back-bonding from the cobalt to the phosphorus and the amidinyl unit.

Concluding Remarks

This work has shown that the ability of the isocyanide compounds $[Cp'Co(CNR)(PMe_3)]$ (Cp' = C_5H_5, C_5Me_5) to undergo [2 + 1], [2 + 2], and [2 + 3] cycloaddition reactions can also be used for the synthesis of the first (carbodiimide)cobalt complexes. Although compounds of the general type $[L_nM(\eta^2\text{-}RN{=}C{=}NR')]$ have already been described for various other transition metals,[6,11,16,17] only the complexes **3**, **6**, and **7**, the related rhodium derivatives reported by Jones,[4] and the (carbodiimide)iridium compounds prepared by Bergman[7] have been obtained by a template route. The reaction of the azide RN_3 with the isocyanide ligand CNR' is strictly regiospecific and leads only to one isomer with the unsymmetrical carbodiimide ligand. The methylation of the complexes $[C_5Me_5Co(\eta^2\text{-}RN{=}C{=}NR')(PMe_3)]$ (**6**, **7**) gives the corresponding cationic amidinylmetal derivatives **8** and **9** in which, as shown by the X-ray crystal structure of **8**, the CoCN three-membered ring still contains a C=N double bond. As metal-bonded carbodiimides have been discussed as unstable intermediates in both catalytic and stoichiometric reactions,[18] it is important to note that the unsymmetrical carbodiimides $PhCH_2N{=}C{=}NPh$ (**10**) and MeN=C=NPh (**11**) can be liberated from the cobalt complexes **3** and **6** under mild conditions on treatment with iodine at room temperature. The yield is 80–85%. We have already reported[3] that from the organometallic byproducts $[Cp'Co(PMe_3)I_2]$ the cyclopentadienyl derivative $[C_5H_5Co(PMe_3)I_2]$ is transformed into the starting isocyanide cobalt compounds $[C_5H_5Co(CNR)(PMe_3)]$ in two steps. Therefore the template synthesis of RN=C=NR' may become useful for those carbodiimides which are difficult to prepare on a classical organic route.

Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting materials **1**,[19] and **4**,[9] were prepared by published methods. Melting points were determined by DTA; conductivity measurements were done in nitromethane. NMR spectra were recorded on Varian EM 360 L, JEOL FX 90 Q, and Bruker AMX 400 instruments; IR spectra, on a Perkin-Elmer 1420 infrared spectrophotometer.

Preparation of $[C_5H_5Co(CNCH_2Ph)(PMe_3)]$ (2). A solution of **1** (248 mg, 0.90 mmol) in 10 mL of benzene was treated at room temperature with an equimolar amount of $CNCH_2Ph$, dissolved in 2 mL of benzene. An immediate color change from dark-brown to red occurred. After the solution was stirred for a few minutes, the solvent was removed in vacuo, and the oily residue was extracted with 10 mL of pentane. Cooling the extract to −78 °C led to the formation of orange-red, extremely air-sensitive crystals which at room temperature gave an oil: yield 243 mg (85%); mp 20 °C dec. Anal. Calcd for $C_{16}H_{21}CoNP$: C, 60.57; H, 6.67; N, 4.42. Found: C, 60.38; H, 6.71; N, 4.44. IR (C_6H_6): $\nu(C{\equiv}N)$ 1860 cm^{-1}. ^1H NMR (C_6D_6, 60 MHz): δ 7.30–6.88 (m, 5 H, C_6H_5), 4.75 (d, *J*(PH) = 0.8 Hz, 5 H, C_5H_5), 4.32 (d, *J*(PH) = 1.4 Hz, 2 H, CH_2), 1.03 (d, *J*(PH) = 9.0 Hz, 9 H, PMe_3).

Preparation of $[C_5H_5Co(\eta^2(C,N(Ph))\text{-}PhCH_2N{=}C{=}NPh)(PMe_3)]$ (3). A solution of **2** (279 mg, 0.88 mmol) in 20 mL of ether was treated at −78 °C with phenyl azide (96 μL, 0.88 mmol). An immediate color change from orange-red to green occurred, accompanied by gas evolution. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo, the residue was repeatedly washed with pentane and then extracted with 30 mL of ether. The ether solution was concentrated to ca. 15 mL in vacuo, and the concentrate was cooled to −78 °C. Green crystals precipitated which were recrystallized from ether: yield 75 mg (21%); mp 77 °C dec. Anal. Calcd for $C_{22}H_{26}CoN_2P$: C, 64.71; H, 6.42; N, 6.86. Found: C, 64.99; H, 6.21; N, 6.62. IR (C_6H_6): $\nu(N{=}C{=}N)$ 1705 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 7.86–6.74 (m, 10 H, C_6H_5), 5.39 (s, 2 H, CH_2), 4.42 (s, 5 H, C_5H_5), 0.60 (d, *J*(PH) = 9.9 Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 161.6 (d, *J*(PC) = 14.1 Hz, N=C=N), 150.1, 143.9, 128.8, 128.6, 127.8, 126.5, 122.0, and 119.6 (all s,

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C_6H_5), 82.2 (d, *J*(PC) = 1.8 Hz, C_5H_5), 60.1 (d, *J*(PC) = 2.7 Hz, CH_2), 17.6 (d, *J*(PC) = 27.7 Hz, PMe_3).

Preparation of [$C_5Me_5Co(CNMe)(PMe_3)$] (5). A solution of 4 (554 mg, 1.60 mmol) in 20 mL of ether was treated at −78 °C with methyl isocyanide (90 μL, 1.60 mmol). An immediate color change from brown to orange-red occurred. After the reaction mixture was warmed to room temperature, the solvent was removed, and the oily residue was extracted with 15 mL of pentane. The extract was brought to dryness in vacuo to give, even after storing at −78 °C for 2 days, an orange-red oil: yield 473 mg (95%). IR (C_6H_6): ν(C≡N) 1854 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 2.81 (d, *J*(PH) = 2.1 Hz, 3 H, NCH_3), 1.95 (d, *J*(PH) = 1.0 Hz, 15 H, C_5Me_5), 1.12 (d, *J*(PH) = 8.2 Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 212.1 (d, br, *J*(PC) = 56.3 Hz, $CNCH_3$), 90.7 (s, $C_5(CH_3)_5$), 29.0 (d, *J*(PC) = 4.0 Hz, $CNCH_3$), 20.6 (d, *J*(PC) = 25.2 Hz, PMe_3), 11.6 (s, $C_5(CH_3)_5$).

Preparation of [$C_5Me_5Co(\eta^2$(*C,N*(Ph))-MeN=C=NPh)(PMe_3)] (6). A solution of 5 (479 mg, 1.54 mmol) in 15 mL of ether was treated at −78 °C with phenyl azide (286 μL, 2.62 mmol). An immediate color change from orange-red to red-brown occurred, accompanied by gas evolution. After the reaction mixture was warmed to room temperature, the solvent was removed in vacuo. The oily residue was washed twice with 5 mL of cold (−78 °C) pentane and then dissolved in 10 mL of ether. The ethereal solution was filtered, and the filtrate was concentrated to ca. 6 mL and cooled to −78 °C. A red-brown microcrystalline solid precipitated, which was filtered off, washed with pentane, and dried in vacuo: yield 366 mg (59%); mp 38 °C dec. Anal. Calcd for $C_{21}H_{32}CoN_2P$: C, 62.68; H, 8.02; N, 6.96. Found: C, 62.99; H, 8.28; N, 7.11. IR (KBr): ν(N=C=N) 1700 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 7.64–6.63 (m, 5 H, C_6H_5), 3.77 (s, 3 H, NCH_3), 1.57 (d, *J*(PH) = 1.4 Hz, 15 H, C_5Me_5), 0.58 (d, *J*(PH) = 8.8 Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 160.6 (d, *J*(PC) = 15.6 Hz, N=C=N), 148.2 (d, *J*(PC) = 1.0 Hz, ipso-C of C_6H_5), 128.6, 120.9, and 118.2 (all s, C_6H_5), 92.7 (d, *J*(PC) = 2.2 Hz, $C_5(CH_3)_5$), 41.0 (d, *J*(PC) = 2.3 Hz, NCH_3), 17.1 (d, *J*(PC) = 24.8 Hz, PMe_3), 10.5 (s, $C_5(CH_3)_5$).

Preparation of [$C_5Me_5Co(\eta^2$(*C,N*(Tol))-MeN=C=NTol)(PMe_3)] (7) was analogous to that described for 6, using 5 (480 mg, 1.54 mmol) and 1.5 mL of a 1.74 M solution of *p*-tolyl azide (2.62 mmol) in ether as starting materials. A red-brown solid was obtained: yield 372 mg (58%); mp 25 °C dec. Anal. Calcd for $C_{22}H_{34}CoN_2P$: C, 63.45; H, 8.23; N, 6.73. Found: C, 63.64; H, 8.37; N, 6.70. IR (KBr): ν(N=C=N) 1701 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 7.55 and 6.99 (both d, AB pattern, *J*(HH) = 8.2 Hz, 4 H, C_6H_4), 3.80 (s, 3 H, NCH_3), 2.12 (s, 3 H, $C_6H_4CH_3$), 1.60 (d, *J*(PH) = 1.2 Hz, 15 H, C_5Me_5), 0.62 (d, *J*(PH) = 8.9 Hz, 9 H, PMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 161.0 (d, *J*(PC) = 15.4 Hz, N=C=N), 145.5, 129.4, 127.0, and 120.9 (all s, C_6H_4), 92.7 (d, *J*(PC) = 1.5 Hz, $C_5(CH_3)_5$), 41.0 (d, *J*(PC) = 1.5 Hz, NCH_3), 20.9 (s, $C_6H_4CH_3$), 17.1 (d, *J*(PC) = 24.6 Hz, PMe_3), 10.5 (s, $C_5(CH_3)_5$).

Preparation of [$C_5Me_5Co(\eta^2$(*C,N*(Ph))-Me_2N=C=NPh)(PMe_3)]PF_6 (8). A solution of 6 (157 mg, 0.39 mmol) in 10 mL of ether was treated at room temperature with excess methyl iodide (50 μL, 0.80 mmol). After the reaction mixture was stirred for 2 h, the mother liquor was removed and the green precipitate washed three times with 5 mL of ether. The solid together with NH_4PF_6 (65 mg, 0.40 mmol) was dissolved in 3 mL of methanol, and the solution was stirred for 30 min at 25 °C. The volatiles were distilled off, and the residue was extracted with 5 mL of CH_2Cl_2. After the extract was brought to dryness in vacuo, the residue was recrystallized from methanol/ether (1:10) to give green crystals: yield 178 mg (81%), dec 166 °C, Λ 77 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{22}H_{35}CoF_6N_2P_2$: C, 46.98; H, 6.27; N, 4.98. Found: C, 47.12; H, 6.16; N, 5.00. IR (KBr): ν(N=C=N) 1696 cm^{-1}. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.44–6.94 (m, 5 H, C_6H_5), 3.90 and 3.26 (both s, 3 H each, NCH_3), 1.68 (d, *J*(PH) = 1.8 Hz, 15 H, C_5Me_5), 1.28 (d, *J*(PH) = 9.8 Hz, 9 H, PMe_3). ^{13}C NMR (CD_3NO_2, 100.6 MHz): δ 172.1 (d, *J*(PC) = 23.7 Hz, N=C=N), 138.2, 130.8, 126.3, and 125.2 (all s, C_6H_5), 95.4 (d, *J*(PC) = 2.1 Hz, $C_5(CH_3)_5$), 45.0 and 42.2 (both s, NCH_3), 16.0 (d, *J*(PC) = 28.4 Hz, PMe_3), 10.1 (s, $C_5(CH_3)_5$).

Table II. Crystallographic Data for 8

formula	$C_{22}H_{35}CoF_6N_2P_2$
fw	562.41
cryst size, mm	0.2 × 0.15 × 0.075
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
cell dimens determn	23 reflcns, 12° < θ < 14°
a, Å	8.786(1)
b, Å	9.067(1)
c, Å	17.938(3)
α, deg	79.73(1)
β, deg	75.82(1)
γ, deg	77.56(1)
V, $Å^3$	1341.2
Z	2
d_{calcd}, g cm^{-3}	1.392
diffractometer	Enraf-Nonius CAD 4
radiation (graphite monochromated)	Mo Kα (0.709 30 Å)
temp, °C	20 ± 1
μ, cm^{-1}	8.1
scan method	ω/θ
2θ(max), deg	46
tot. no. of reflcns scanned	3984
no. of unique reflcns	3699
no. of obsd reflcns ($F_o > 3\sigma(F_o)$)	2437
no. of params refined	336
R	0.047
R_w	0.051
reflex/param ratio	7.25
resid electron density, e $Å^{-3}$	+0.565/−0.257

Preparation of [$C_5Me_5Co(\eta^2$(*C,N*(Tol))-Me_2N=C=NTol)(PMe_3)]PF_6 (9) was analogous to that described for 8, using 6 (162 mg, 0.39 mmol), methyl iodide (50 μL, 0.80 mmol), and NH_4PF_6 (65 mg, 0.40 mmol) as starting materials. After recrystallization from methanol/ether (1:10) a green crystalline solid was obtained: yield 178 mg (79%), dec 171 °C, Λ 79 $cm^2\ \Omega^{-1}\ mol^{-1}$. Anal. Calcd for $C_{23}H_{37}CoF_6N_2P_2$: C, 47.92; H, 6.47; N, 4.86. Found: C, 47.50; H, 6.45; N, 4.77. IR (KBr): ν(N=C=N) 1677 cm^{-1}. ^1H NMR (CD_3NO_2, 90 MHz): δ 7.14 and 6.89 (both d, AB pattern, *J*(HH) = 8.3 Hz, 4 H, C_6H_4), 3.88 and 3.23 (both s, 3 H each, NCH_3), 2.25 (s, 3 H, $C_6H_4CH_3$), 1.67 (d, *J*(PH) = 2.0 Hz, 15 H, C_5Me_5), 1.27 (d, *J*(PH) = 9.8 Hz, 9 H, PMe_3). ^{13}C NMR (CD_3NO_2, 100.6 MHz): δ 170.9 (d, *J*(PC) = 24.1 Hz, N=C=N), 135.4, 135.0, 131.4, and 126.4 (all s, C_6H_4), 95.3 (d, *J*(PC) = 2.3 Hz, $C_5(CH_3)_5$), 45.0 and 41.9 (both s, NCH_3), 21.1 (s, $C_6H_4CH_3$), 16.0 (d, *J*(PC) = 28.2 Hz, PMe_3), 10.1 (s, $C_5(CH_3)_5$).

Preparation of PhN=C=NCH$_2$Ph (10) from 3. A solution of 3 (98 mg, 0.24 mmol) in 15 mL of ether/benzene (2:1) was treated at room temperature with a solution of I_2 (61 mg, 0.24 mmol) in 5 mL of ether. A dark solid of [$C_5H_5Co(PMe_3)I_2$] precipitated which after 15 min was filtered off and washed with ether. The filtrate was evaporated to dryness in vacuo, and the oily residue was extracted with 10 mL of pentane. After the solvent was removed, 10 was obtained as an almost colorless oil: yield 40 mg (80%). Compound 10 was described in the literature,[20] but no spectroscopic data were given. MS (70 eV): *m/z* 208 (11, M^+), 91 (100, $C_6H_5CH_2^+/C_6H_5N^+$). IR (C_6H_6): ν(N=C=N) 2128 cm^{-1}. ^1H NMR (C_6D_6, 60 MHz): δ 7.15–6.83 (m, 10 H, C_6H_5), 4.03 (s, 2 H, CH_2).

Preparation of MeN=C=NPh (11) from 6 was analogous to that described for 10, using 6 (95 mg, 0.24 mmol) and an equimolar amount of I_2 as starting materials. A colorless oil was obtained: yield 26 mg (84%). A procedure for compound 11 was already reported.[21] MS (70 eV): *m/z* 132 (100, M^+), 117 (5, $M^+ - CH_3$), 103 (6, $C_6H_5NC^+$). IR (pentane): ν(N=C=N) 2142 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 7.50–7.00 (m, 5 H, C_6H_5), 3.23 (s, 3 H, CH_3).

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Table III. Positional Parameters and Esd's for 8

atom	x	y	z	B_{eq}[a] (Å^2)
Co	0.2024(1)	0.29629(9)	0.23126(4)	3.04(2)
P1	0.3992(2)	0.2112(2)	0.1386(1)	4.74(4)
P2	−0.500	0.500	0.500	3.53(5)
P2*	0.000	0.000	0.000	4.79(6)
F1	−0.5344(5)	0.4357(5)	0.5896(2)	6.3(1)
F2	−0.6181(6)	0.6503(5)	0.5199(3)	8.3(1)
F3	−0.6409(5)	0.4294(6)	0.4915(3)	9.0(1)
F4	0.1670(5)	−0.0447(6)	0.0237(3)	9.0(1)
F5	0.0799(7)	0.0929(8)	−0.0744(3)	12.1(2)
F6	0.0389(7)	−0.1422(6)	−0.0415(4)	12.3(2)
N1	0.1662(6)	0.0916(5)	0.2777(3)	4.1(1)
N2	0.3604(6)	0.0799(6)	0.3540(3)	4.6(1)
C1	0.2690(7)	0.1362(7)	0.3029(3)	3.8(1)
C2	0.3686(9)	−0.0761(8)	0.3946(5)	7.0(2)
C3	0.4739(8)	0.1646(8)	0.3656(4)	6.3(2)
C4	0.0532(7)	−0.0027(6)	0.3031(4)	3.8(1)
C5	−0.0019(8)	−0.0530(7)	0.2471(4)	6.1(2)
C7	−0.1678(9)	−0.1941(9)	0.3451(5)	7.0(2)
C8	−0.1199(9)	−0.1433(9)	0.4014(5)	7.0(2)
C9	−0.0109(8)	−0.0453(8)	0.3802(4)	5.3(2)
C10	0.465(1)	0.0066(9)	0.1506(5)	8.3(3)
C11	0.370(1)	0.246(1)	0.0394(4)	8.1(3)
C12	0.5822(9)	0.2800(9)	0.1284(5)	7.7(2)
C13	−0.0311(7)	0.4148(7)	0.2610(4)	4.0(2)
C14	−0.1794(8)	0.3501(9)	0.2871(5)	6.2(2)
C15	0.0385(7)	0.4668(7)	0.1837(3)	4.1(1)
C16	−0.0329(9)	0.475(1)	0.1135(4)	7.2(2)
C17	0.1771(8)	0.5242(7)	0.1840(4)	4.3(2)
C18	0.272(1)	0.6123(8)	0.1171(4)	6.8(2)
C19	0.1902(7)	0.5093(6)	0.2627(4)	4.0(1)
C20	0.3091(8)	0.5728(7)	0.2896(4)	6.6(2)
C21	0.0637(7)	0.4409(7)	0.3099(3)	3.9(1)
C22	0.025(1)	0.4063(9)	0.3976(4)	6.3(2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

X-ray Structural Analysis of 8. Single crystals were grown by diffusion of ether into a saturated solution of 8 in methanol. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scan method) was applied; the minimal transmission was 94.17%. The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates (see Table III) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (unit weights). The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by the riding method. All calculations were performed on a Micro-VAX computer using the program package SDP[22] from Enraf-Nonius. For other details, see Table II.

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Supplementary Material Available: An ORTEP drawing of complex 8, showing the atom-numbering scheme, and tables of crystal data, bond distances, bond angles, least-squares planes, positional parameters, and general displacement expressions (12 pages). Ordering information is given on any current masthead page.

OM920834T

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