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Cobalt Metallocycles. VII.[1] η^5-Cyclopentadienyl-η^4-iminocyclopentadienecobalt Complexes from a Reaction of Cobaltacyclopentadienes with Isocyanides

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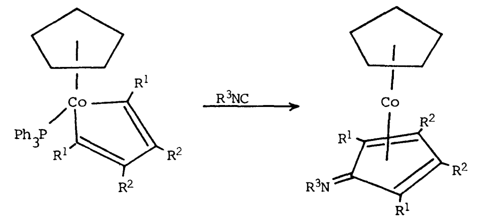
Synopsis. The reaction of (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadienes with isocyanides gives η^5-cyclopentadienyl-η^4-iminocyclopentadienecobalt complexes in good yields. Treatment of the product with HBF_4 or CH_3I yields the corresponding aminocobalticinium salt.

Cyclopentadienone–metal complexes have been isolated and characterized from the reactions of metal carbonyls with alkynes and direct reaction with substituted cyclopentadienones.[2] However, few examples of the imino analog *i.e.* iminocyclopentadiene–metal complexes are known. Weiss and Hubel reported that $Fe(CO)_5$ reacts with phenyliminotetraphenylcyclopentadiene to yield an iron tricarbonyl complex.[3] More recently, *t*-butylimino-tetrakis(trifluoromethyl)cyclopentadiene complexes of Mo and W have been reported.[4] Previous work in this laboratory has shown that carbon monoxide reacts with (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadienes (**1**) to afford the cyclopentadienone complexes. Consequently it has been predicted that isocyanides would be incorporated into the ring. The synthetic procedure for the preparation of iminocyclopentadienecobalt has the advantage that substituents can be introduced into the iminocyclopentadiene ring, since the parent cobaltacyclopentadienes with corresponding substituents are readily accessible.[5] Some reactions of the obtained iminocyclopentadiene–cobalt complexes are reported, which indicate the strong polarization of the coordinated iminocyclopentadiene ring.

A benzene solution of (η^5-cyclopentadienyl)(triphenylphosphine)tetraphenylcobaltacyclopentadiene (**1a**) and *t*-butyl isocyanide when heated at 70 °C gradually turned dark-brown, and crystals of **2a** (air stable) were isolated in good yield. IR, NMR, and elemental analysis, indicated **2a** to be (η^5-cyclopentadienyl)(η^4-*t*-butyliminotetraphenylcyclopentadiene)cobalt. Other cobaltacyclopentadiene complexes similarly reacted with isocyanides, but higher temperatures were required to complete reaction due to the presence of electron withdrawing substituents in the cobalt metallocycles. The complexes are summarized in Table 1.



(1)

1a $R^1,R^2=Ph$
1b $R^1=Ph, R^2=Me$
1c $R^1=Ph, R^2=CO_2Me$

2a—2e

The iminocyclopentadiene ligand in these complexes is strongly coordinated to the cobalt. An attempt to liberate the coordinated iminocyclopentadiene in **2c** by carbon monoxide (40 atm, 120 °C) resulted in the formation of a small amount of the desired product, most of the complex remaining unreacted.

In the iminocyclopentadiene–cobalt complexes, by analogy with the cyclopentadienone analogs,[6] an ionic resonance contribution **2′** may be expected. In agreement with this expectation, the ν(C=N) absorption in 2,6-xylyliminotetraphenylcyclopentadiene (1630 cm^{-1}) was markedly reduced on coordination to cobalt (1575 cm^{-1}).

Furthermore, complex **2** readily forms aminocobalticinium salts (**3**) on protonation and methylation (Eq. 2). The protonation by fluoroboric acid was performed by shaking a benzene solution of **2** with the acid. The ν(C=N) peak was absent in the IR spectrum of the resulting complex while the ν(N–H) appeared at 3300—

TABLE 1. IMINOCYCLOPENTADIENE–COBALT COMPLEXES

	Compound			Yield (%)	Mp (°C)	Found (Calcd) %			NMR[a)] δ (ppm)		IR[b)] ν(C=N) (cm^{-1})
	R^1	R^2	R^3			C	H	N	η-C_5H_5	CH_3	
2a	Ph	Ph	*t*-Bu	84	213—215	81.26 (80.98	6.12 6.08	2.58 2.49)	4.71	1.27	1580
2b	Ph	Ph	*p*-MeC_6H_4	49	166—168	82.37 (82.40	5.52 5.40	2.24[c)] 2.34)	4.60	2.12	1555
2c	Ph	Ph	2,6-$Me_2C_6H_3$	86	250—251	82.75 (82.47	5.46 5.60	2.18 2.29)	4.58	1.88, 2.59 (3H) (3H)	1575
2d	Ph	Me	2,6-$Me_2C_6H_3$	79	211—212	79.36 (78.84	6.44 6.20	2.78 2.87)	4.29	1.69, 1.89, 2.67 (3H) (6H) (3H)	1565
2e	Ph	CO_2Me	2,6-$Me_2C_6H_3$	67	178—179	70.89 (70.95	5.23 5.25	2.38 2.43)	4.97	1.51, 2.47, 3.81[d)] (3H) (3H) (6H)	1575

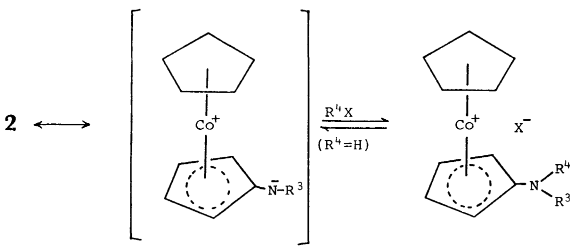
a) In C_6D_6. b) KBr disk. c) Solvated with C_6H_6. d) In $CDCl_3$.

Table 2. Cobalticinium salts

	Compound			Mp (°C)	Found (Calcd) (%)				NMR[a)] δ (ppm)				IR[b)] ν(N–H) (cm^{-1})
	R^3	R^4	X		C	H	N	I	η-C_5H_5	C–CH_3	N–CH_3	N–H	
3a	*t*-Bu	H	BF_4	277—282	70.25 (70.06	5.40 5.42	2.12 2.15)		5.54	1.08		4.02	3375
3b	2,6-$Me_2C_6H_3$	H	BF_4	290—293	72.08 (72.12	5.08 5.04	1.98 2.00)		5.50	1.82 2.48		6.22	3350
3c	*t*-Bu	Me	I	275—277	66.71 (66.39	5.11 5.29	2.02 1.99	18.05 17.99)	5.78	0.99	2.80		
3d	*p*-Me–C_6H_4	Me	I	303—304	70.65 (70.51	5.07 5.05	1.78 1.71	15.55 15.52)	5.80	2.02	3.33		

a) In $CDCl_3$. b) KBr disk.

3400 cm^{-1}. On shaking the fluoroborate salt with alkali, smooth deprotonation occurred yielding the parent neutral complex (**2**). *N*-Methylated cobalticinium salts were obtained when **2a** and **2b** were treated with iodomethane. **2c** did not react with iodomethane possibly due to steric hindrance around the N atom. The cyclopentadienyl proton resonances shifted from δ 4.58—4.71 in **2a**—**2c** to δ 5.49—5.79 ppm in **3a**—**3d**, in accord with the increase of oxidation number of the cobalt.



(2)

2′ **3**

R^4=H or Me
X=BF_4 or I

Experimental

IR spectra were recorded on a Shimadzu IR-27G and NMR spectra on a Varian HA-100 spectrometer. Melting points were determined on a Mitamura micro-melting point apparatus. (η^5-Cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes were prepared by the methods reported.[5)]

Preparation of (η^5-Cyclopentadienyl)(η^4-iminocyclopentadiene)cobalt. A solution of **1a** (0.742 g, 1.0 mmol) and *t*-BuNC (0.4 ml) in benzene (10 ml) was heated at 70 °C for 8 h. The volume of the solvent was reduced *in vacuo* and hexane added to give black crystals of **2a** (0.473 g).

Similar treatment of cobaltacyclopentadiene complexes with isocyanides gave the corresponding iminocyclopentadiene–cobalt complexes (Table 1). Preparation of **2e** was conducted at 130 °C.

*Reaction of **2c** with Carbon Monoxide.* A solution of **2c** (0.122 g, 0.2 mmol) in benzene (20 ml) was placed in an autoclave and carbon monoxide introduced (40 atm). After heating at 120 °C for 8 h, the solution was concentrated. The addition of hexane afforded the starting cobalt complex (0.06 g, 49% recovery). The mother liquid was chromatographed on alumina and a red fraction eluted with benzene/hexane (1: 1). Evaporation of the solvent, followed by crystalization from hexane gave dark-red crystals of 2,6-xylyliminotetraphenylcyclopentadiene (0.018 g, 18%), mp 190 °C. Found: C, 91.11; H, 6.03; N, 2.79%; mol wt, 487 (mass spectrum). Calcd for $C_{37}H_{29}N$: C, 91.13; H, 5.99; N, 2.87%; mol wt, 487. NMR ($CDCl_3$): δ 1.99 (s, 9H); 6.5—7.2 (multiplet, Ph protons) ppm. IR (KBr): ν(C=N), 1630 cm^{-1}.

*Reaction of **2** with Fluoroboric Acid.* To a solution of **2a** (0.10 g, 0.18 mmol) in benzene (10 ml) was added a few drops of fluoroboric acid (42 %, aq solution). The mixture turned pale immediately after shaking and an orange-red solid precipitated. Extraction of the solid with a small amount of CH_2Cl_2 followed by the addition of benzene gave red crystals of **3b** (0.083 g, 73%). **3a** was similarly prepared (46%). The physical properties of the complexes are summarized in Table 2.

*Reaction of **2** with Iodomethane.* A solution of **2a** (0.056 g, 0.1 mmol) and iodomethane (0.2 ml) in benzene (10 ml) was left overnight at room temperature. The resulting dark red-brown solution was concentrated *in vacuo* to give dark red brown crystals of **3c** (0.063 g, 89%). **3d** was similarly obtained.

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