BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2743—2744 (1978)

Cyclopentadienyl- and Pentamethylcyclopentadienylbis(isocyanide)cobalt(I)[1]

Yasuhiro YAMAMOTO,* Takaya MISE, and Hiroshi YAMAZAKI
The Institute of Physical and Chemical Research, Wako-shi, Saitama 351

(Received February 28, 1978)

Synopsis. Compounds, η-$C_5H_5Co(RNC)_2$ and η-$Me_5C_5Co(RNC)_2$ were prepared from $Co_2(RNC)_8$ and C_5R_5H (R=H, CH_3), and from η-$C_5H_5Co(CO)_2$ and isocyanide.

The cobalt complexes having cyclopentadienyl or pentamethylcyclopentadienyl group as a ligand, η-$C_5H_5CoL_2$ (L=CO,[2] phosphorus ligands[3]) η-$Me_5C_5Co(CO)_2$[4] and η-$C_5H_5Co(CO)L$ (L=PPh_3,[5] RNC[6]) have been known. The chemical reactions of these complexes have been widely provided. However, analogous η-$R_5C_5Co(RNC)_2$ has not been known yet. We here report the preparation and reactions of this type of complexes.

The two methods for the preparation are; (1) the reaction of octakis(isocyanide)dicobalt(0) with cyclopentadiene or pentamethylcyclopentadiene, and (2) the reactions of η-$C_5H_5Co(CO)_2$ with isocyanide. The reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with cyclopentadiene in toluene at 120 °C gave two products, dark brown complex **1a** formulated as η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)_2$ and unknown brown organic compound **2**[7] formulated as $(C_5H_6)(C_9H_9N)_4$.

$$Co_2(RNC)_8 + C_5H_6 \rightarrow \eta\text{-}C_5H_5Co(RNC)_2 + (C_5H_6)(RNC)_4. \tag{1}$$

The chemical shifts of the *ortho*-methyl resonances of coordinated isocyanides were independent of the concentration of free 2,6-$Me_2C_6H_3NC$ added in the NMR spectra of η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)_2$, suggesting the absence of dissociation. When $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ was treated with pentamethylcyclopentadiene, only η-$Me_5C_5Co(2,6\text{-}Me_2C_6H_3NC)_2$ **1b** was formed.

The reaction of η-$C_5H_5Co(CO)_2$ or η-$Me_5C_5Co(CO)_2$ with excess 2,6-xylyl isocyanide proceeded with substitution of a carbon monoxide at room temperature to give η-$R_5C_5Co(CO)$ (2,6-$Me_2C_6H_3NC$) (**3a**: R=H, **3b**: R=CH_3) (Eq. 2). Upon heating at 120 °C, the further displacement of CO took place to afford **1a**, although no displacement of CO occurred in the case of pentamethylcyclopentadienyl analog. This is due to the results that back-bonding Co(3d)→C≡O(π*) in **3b** is more extensive than that in **3a**, as shown in the C≡O stretching frequencies of **3a** (1956 cm⁻¹) and **3b** (1924 cm⁻¹) (Table 1).

Compounds **3a** and **3b** were regenerated together with a small amount of η-$R_5C_5Co(CO)_2$, when **1a** and **1b** were treated with CO (Eq. 3). These reactions were formally reversible.

$$\eta\text{-}C_5H_5Co(CO)_2 + RNC \rightarrow \eta\text{-}C_5R_5(CO)(RNC) + CO \tag{2}$$

$$\eta\text{-}C_5H_5Co(CO)(RNC) + RNC \rightleftharpoons \eta\text{-}C_5H_5Co(RNC)_2 + CO \tag{3}$$

Compound **1c** was also prepared from η-$C_5H_5Co(CO)_2$ and mesityl isocyanide. However, when η-$C_5H_5Co(CO)_2$ was treated with aliphatic isocyanides such as *t*-butyl or cyclohexyl isocyanide under similar conditions, one mole of CO was substituted to produce η-$C_5H_5Co(CO)(RNC)$,[6] without producing bis(isocyanide) derivative.

Table 1. Infrared spectra cf **1** and **3**

	Compound	IR (cm⁻¹)[a]	
		ν(N≡C)	ν(C≡O)
1a	η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)_2$	2068 1990	
1b	η-$C_5Me_5Co(2,6\text{-}Me_2C_6H_3NC)_2$	2052 1942	
1c	η-$C_5H_5Co(2,4,6\text{-}Me_3C_6H_2NC)_2$	2053 1989	
3a	η-$C_5H_5Co(CO)(2,6\text{-}Me_2C_6H_3NC)$	2075	1956
3b	η-$C_5Me_5Co(CO)(2,6\text{-}Me_2C_6H_3NC)$	2038	1924

a) Measured in benzene.

The reaction of **1a** with iodine in a 1:1 molar ratio took place readily to give [η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)I$]I, and that with an excess of iodine gave [η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)_2I$]$I_3$. The similar type of complex, [η-$Me_5C_5Co(2,6\text{-}Me_2C_6H_3NC)_2I$]$I_3$, was also obtained from **1b** and iodine.

Compound **1a** reacted readily with TCNE to give the olefin complex η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)$(TCNE), whereas no reaction occurred on treatment with dialkyl maleate. When **1a** was treated with azobenzene at 120 °C, the reaction led to recovery of **1a**, contrasted with the reaction leading to the formation of η-$C_5H_5Co(o\text{-}N(Ph)NHC_6H_4)$ from η-$C_5H_5Co(CO)_2$[8] or η-$C_5H_5Co(CO)(t\text{-}BuNC)$ and azobenzene.

The relatively low reactivity of η-$C_5H_5Co(RNC)_2$ may be due to the steric hindrance and no dissociation of ligands.

Experimental

*Preparation of η-$Me_5C_5Co(2,6\text{-}Me_2C_6H_3NC)_2$ **1b** from $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$[9] and Me_5C_5H.* A mixture of pentamethylcyclopentadiene (0.45 ml, 2.65 mmol) and $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$, prepared from $Co_2(CO)_8$ (0.18 g, 0.53 mmol) and 2,6-$Me_2C_6H_4NC$ (0.69 g, 5.3 mmol), *in situ* was heated in toluene at 120 °C. After 4 h, the solvent was removed in vacuo and the residue was chromatographed on alumina. Eluting with hexane–benzene (1:1) gave dark red crystals of η-$Me_5C_5Co(2,6\text{-}Me_2C_6H_3NC)_2$ **1b** (0.175 g, 36%, mp (N_2) ≈108 °C(dec)), which was crystallized from hexane at −30 °C. NMR(C_6H_5Cl): δ 1.95 (bs, Me_5C_5) and 2.25 (bs, 12H, CH_3). Found: C, 73.13; H, 7.34; N, 6.05%. Calcd for $C_{28}H_{33}N_2Co$: C, 73.67; H, 7.29; N, 6.14%.

*Preparation of η-$C_5H_5Co(2,6\text{-}Me_2C_6H_3NC)_2$ **1a** from η-$C_5H_5Co(CO)_2$ and 2,6-Xylyl Isocyanide.* A mixture of η-$C_5H_5Co(CO)_2$ (0.90 g, 5.0 mmol) and 2,6-xylyl isocyanide (2.0 g, 1.53 mmol) in toluene (15 ml) was heated at 120 °C. After

6 h, the solvent was removed in vacuo and the residue was chromatographed on alumina, using hexane-benzene (1:1). The solvent was removed in vacuo, and the brown residue was crystallized from hexane at −30 °C to afford the title complex (1.7 g, 88%, mp(N_2) 94—97 °C(dec)). Mass spectrum M^+ 386 (386.39) Found: C, 71.49; H, 6.01; N, 7.26%. Calcd for $C_{23}H_{23}N_2Co$: C, 71.50; H, 6.00; N, 7.25%. Compound **1c** (72%; mp 72—74 °C(dec)) was prepared from η-$C_5H_5Co(CO)_2$ and mesityl isocyanide by the procedure similar to the method (2). Found: C, 72.41; H, 6.58; N, 6.81%. Calcd for $C_{25}H_{27}N_2Co$: C, 72.45; H, 6.57; N, 6.76%.

Preparation of η-$C_5H_5Co(CO)$ (2,6-$Me_2C_6H_3NC$). A mixture of η-$C_5H_5Co(CO)_2$ (0.18 g, 1.0 mmol) and 2,6-xylyl isocyanide (0.30 g, 2.3 mmol) in toluene (15 ml) was kept at room temperature for 5 h. The work-up of the reaction mixture gave the title compound (0.25 g, 92%, mp 70—71 °C(dec)). Mass M^+ 283(283.22). Found: C, 63.52; H, 4.89; N, 5.03%. Calcd for $C_{15}H_{14}OCo$: C, 63.61; H, 4.92; N, 4.95%.

Reaction of η-R_5C_5Co(2,6-$Me_2C_6H_3NC)_2$. *a) With Iodine*: To a solution of η-C_5H_5Co(2,6-$Me_2C_6H_3NC)_2$ (0.09 g, 0.23 mmol) in benzene (5 ml) was added iodine (0.09 g, 0.35 mmol) in benzene (5 ml) at room temperature. After 45 min, the resulting black brown crystals (0.065 g, 44%; mp 143—145 °C (dec)) were filtered off, which were crystallized from CH_2Cl_2-hexane. The complex contains one molecule of CH_2Cl_2 in crystallization. IR(KBr): 2189 (N≡C) cm^{-1}. NMR($CDCl_3$): δ 2.54 (s, CH_3) 6.27 (bs, C_5H_5), and 7.16 (bs, C_6H_3) ppm. Found: C, 40.19; H, 3.33; N, 3.97%. Calcd for $C_{24}H_{25}N_2Cl_2I_2Co$: C, 39.75; H, 3.48; N, 3.86%.

[η-C_5H_5Co(2,4,6-$Me_3C_6H_2NC)_2I$]I (83%, mp ≈160 °C (dec)) was prepared by the procedure similar to that mentioned above. IR(KBr): 2178 (N≡C) cm^{-1}. NMR($CDCl_3$): δ 2.33 (s, *p*-Me), 2.51 (s, *o*-Me) 6.30 (bs, C_5H_5) and 6.92 (s, C_6H_2) ppm. Found: C, 44.70; H, 4.02; N, 4.26%. Calcd for $C_{25}H_{27}N_2I_2Co$: C, 44.94; H, 4.07; N, 4.19%.

[η-Me_5C_5Co(2,6-$Me_2C_6H_3NC)_2I$]I_3 (mp 166—168 °C(dec)) was obtained from **1b** and an excess of I_2 in hexane. IR(KBr): 2151 and 2165 (N≡C) cm^{-1}. NMR($CDCl_3$): δ 2.21 (s, Me_5C_5), 2.47 (s, *o*-Me), and *ca.* 7.18 (m, C_6H_3). Found: C, 34.85; H, 3.46; N, 2.67; I, 51.40%. Calcd for $C_{28}H_{33}N_2I_4Co$: C, 34.88; H, 3.45; N, 2.91; I, 52.62%.

[η-C_5H_5Co(2,6-$Me_2C_6H_3NC)_2I$]I_3 (mp 105 °C (dec)). IR(KBr): 2185 (N≡C) cm^{-1}. Found: C, 30.14; H, 2.54; N, 3.01%. Calcd for $C_{23}H_{23}N_2I_4Co$: C, 30.90; H, 2.59; N, 3.13%.

b) With Tetracyanoethylene (TCNE): A solution of TCNE (0.04 g, 0.31 mmol) in benzene (3 ml) was added to a solution of **1a** (0.12 g, 0.31 mmol) in benzene (5 ml) at room temperature and stirred for 1 h. The mixture was chromatographed on alumina. Eluting with CH_2Cl_2 gave brown crystals of η-C_5H_5Co(2,6-$Me_2C_6H_3NC$)(TCNE) (0.46 g, 39%, mp >300 °C). IR(benzene): 2220 (C≡N) and 2152 (N≡C) cm^{-1}. Found: C, 62.43; H, 3.69; N, 18.35%. Calcd for $C_{20}H_{14}N_5Co$: C, 62.67; H, 3.68; N, 18.27%.

The work was partially supported by the Ministry of Education of Japan (Grant No. 264162) (Y.Y.).

References

1) Studies on interactions of isocyanide with transition metal complexes 17. For preceding paper in this series, see Y. Yamamoto and H. Yamazaki, *J. Org. Chem.*, **42**, 4136 (1977).

2) (a) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); (b) A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **82**, 1392 (1961).

3) (a) H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **44**, 2260 (1971); (b) H. Yamazaki and Y. Wakatsuki, *J. Organomet. Chem.*, **139**, 157 (1977); (c) V. Harder, J. Müller and H. Werner, *Helv. Chim. Acta*, **54**, 1 (1971).

4) R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, **8**, 287 (1967).

5) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).

6) Y. Yamamoto and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **27**, 109 (1970).

7) The structure is unknown.

8) T. Joh, N. Hagihara, and S. Murahashi, *Bull. Chem. Soc. Jpn.*, **40**, 661 (1967).

9) Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*, **137**, C31 (1977).