

Cobalt-catalyzed Preparation of Diiminofuran Derivatives
through Double Insertion of Isocyanide into a Metal-Carbon Bond¹⁾

Kazuyoshi SUGANO, Tomoaki TANASE, Kimiko KOBAYASHI,[†]
and Yasuhiro YAMAMOTO*

Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274

[†]RIKEN(The Institute of Physical and Chemical Research), Wako, Saitama 351

The reaction of 2-bromoacetophenone with XylNC (Xyl = 2,6-xylyl) in the presence of Et₃N and cobalt complex such as Co₂(XylNC)₈, CoBr₂(XylNC)₄, [Co(XylNC)₅](PF₆) or Co(acac)₃, gave 2,3-bis-N-(2',6'-xylyl)imino-5-phenyl-2,3-dihydrofuran. The structure was confirmed by an X-ray crystallographic analysis.

The chemistry of dicobalt octacarbonyl has been well documented.²⁾ Dicobalt octaisocyanide with an isoelectronic structure has been expected to have similar behavior from chemical diversity of Co₂(CO)₈, but there are a few reports on the zerovalent isocyanide complex.³⁾ Previously, we have reported that isocyanide reacted with azo compound and active methylene compounds, malonic ester and cyanoacetate, to give indazoline and indazole derivatives and cyclic imino compounds.^{4,5)} These reactions have proceeded via the single or multiple insertion of isocyanide into metal-carbon bonds.

Recently, we have described that the reaction of Co₂(RNC)₈ with carbon polyhalides and benzyl bromide produced indolenine and tetraiminohexane derivatives.⁶⁾ Herein, we wish to report a preparation of diiminofuran derivatives from the cobalt-catalyzed reaction of 2-bromoacetophenone with XylNC (Xyl = 2,6-xylyl).

A mixture of 2-bromoacetophenone (1a), XylNC, and Co₂(XylNC)₈ was refluxed in toluene. After 6 h, the deep red solution was chromatographed on alumina to give reddish orange crystals formulated as (XylNC)₂(C₆H₅COCH) (2a) in a few yield.⁷⁾ When this reaction was carried out in the presence of triethylamine, the reaction proceeded catalytically

and formation of $[\text{Et}_3\text{NH}]\text{Br}$ was observed. This compound (2a) was obtained by using Co(I) , Co(II) , or Co(III) complex as a catalyst, and the turn over number (TON) was enhanced in comparison with that by $\text{Co}_2(\text{XylNC})_8$ (Table 1).

The infrared spectrum of 2a indicated the presence of C=N and C=C bonds at 1707, 1596, and 1581 cm^{-1} . The ^1H NMR spectrum showed three singlets at δ 2.13, 2.25, and 5.93, the latter was assigned to an olefinic proton and others to o-methyl ones. To clarify the structure of 2a, an X-ray crystallographic analysis was undertaken (Fig. 1).⁸⁾ The compound (2a) has a furan ring, $[\text{O(1)C(2)C(1)C(3)C(4)}]$, involving two N-arylimino groups at α and β positions. The furan ring is planar, and N-xylyl groups are nearly perpendicular to the ring, with dihedral angles of $72.9(2)$ and $83.7(2)^\circ$. 4'-Substituted 2-bromoacetophenone (1b: 4'-Me; 1c: 4'-MeO, 1d: 4'-Ph, 1e: 4'-NO₂) also afforded 2,3-bis-N-(2',6'-xylyl)imino-5-(4'-R'-phenyl)-2,3-dihydrofuran ($\text{R}' = \text{2b: Me; 2c: MeO; 2d: Ph; 2e: NO}_2$),⁹⁾ but their yields were low. Any systematic effects of 4'-substituents were not observed (Table 1).

In an attempt to investigate the catalytic species, NH_4PF_6 was added to the solution after the catalytic reaction was over. $[\text{Co}(\text{XylNC})_5](\text{PF}_6)$ was isolated in a good yield, suggesting the presence of a Co(I) species in the reaction. When $\text{CoBr}_2(\text{XylNC})_4$ or $\text{Co}(\text{acac})_3$ was treated with XylNC in the presence of Et_3N and NH_4PF_6 ,

$[\text{Co}(\text{XylNC})_5](\text{PF}_6)$ was obtained quantitatively. These results suggested the presence of a cobalt(I) isocyanide complex as an active species in the catalytic system. A plausible mechanism is proposed in Scheme 1. The

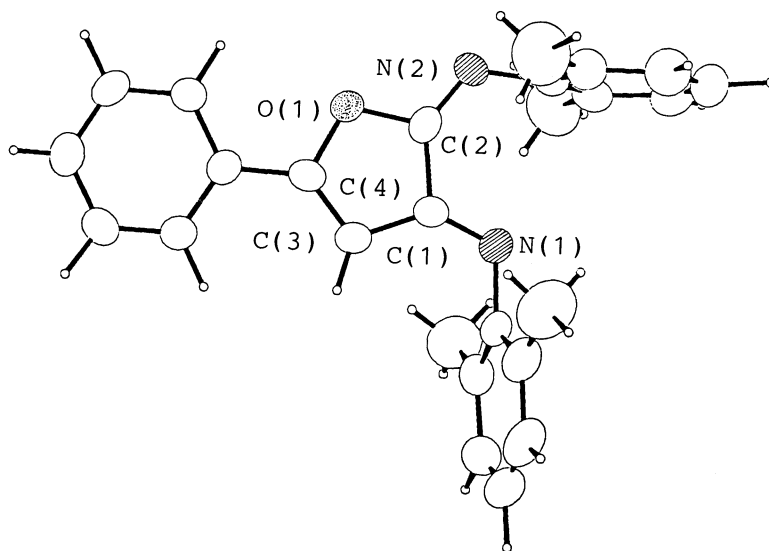
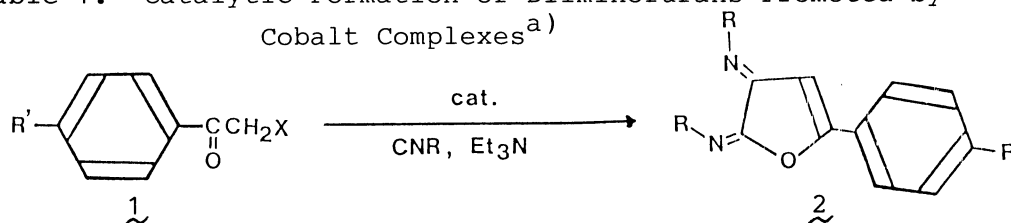


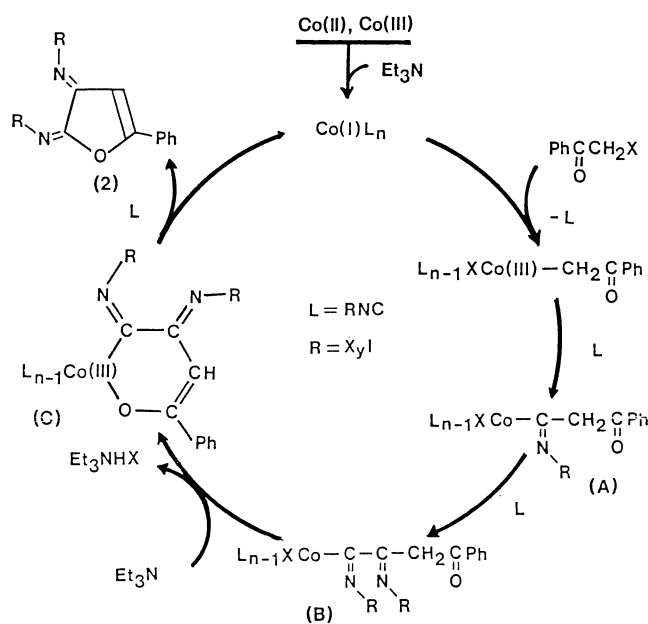
Fig. 1. An ORTEP drawing of 2a. Selected bond distances ($\text{\AA}$) and angles ($^\circ$); O(1)-C(2) 1.396(8), O(1)-C(4) 1.386(6), N(1)-C(1) 1.284(8), N(2)-C(2) 1.247(6), C(1)-C(2) 1.506(9), C(1)-C(3) 1.435(7), C(3)-C(4) 1.347(9), C(2)-O(1)-C(4) $107.4(5)$, C(2)-C(1)-C(3) $104.8(5)$, O(1)-C(2)-C(1) $106.8(4)$, C(1)-C(3)-C(4) $108.0(5)$, O(1)-C(4)-C(3) $113.0(5)$.

Table 1. Catalytic Formation of Diiminofurans Promoted by Cobalt Complexes^{a)}

Run	Catalyst	R'	Product	Yield/% ^{b)}	Turn over
1	Co ₂ (XylNC) ₈	H	2a	11	2.8
2	Co(acac) ₃	H	2a	27	14.6
3	CoBr ₂ (XylNC) ₅	H	2a	23	11.8
4	Co(XylNC) ₅ PF ₆	H	2a	21	10.4
5	CoBr ₂ (XylNC) ₄	H	2a	30	15.0
6	CoBr ₂ (XylNC) ₄	Me	2b	14	6.6
7	CoBr ₂ (XylNC) ₄	MeO	2c	4	1.7
8	CoBr ₂ (XylNC) ₄	Ph	2d	7	3.7
9	CoBr ₂ (XylNC) ₄	NO ₂	2e	5	2.3

a) The reactions were carried out in refluxing toluene for 6 h. Molar ratio of (4'-R')-2-bromoacetophenone/XylNC/Et₃N/catalyst is 50/100/150/1. b) Determined by HPLC.¹⁰⁾ Calculated on a cobalt metal.

reaction consists of an initial reduction of the Co(II) or Co(III) complex to cobalt(I) species. Oxidative addition of 2-bromoacetophenone to the Co(I) species occurred. The subsequent double insertion of isocyanide molecules into the cobalt-carbon bond gave an intermediate (B). Then, 2,3-diimino-5-aryl-2,3-dihydrofuran (2) was formed by reductive elimination from a cobaltacycle (C), regenerating the Co(I) species.



Scheme 1.

References

- 1) Organic Synthesis by Low-Valent Isocyanide Complexes. 6. For preceding paper, see: T. Hagiwara, K. Taya, Y. Yamamoto, and H.

- Yamazaki, J. Mol. Cat., 54, 165(1989).
- 2) For example, J. Falbe, "Carbon Monoxide in Organic Synthesis," Springer-Verlag, West Berlin (1970).
 - 3) Y. Yamamoto and H. Yamazaki, J. Organomet. Chem., 137, C31(1977); Y. Yamamoto and H. Yamazaki, Inorg. Chem., 17, 3111(1978); G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, J. Chem. Soc., Chem. Commun. 1977, 256; W. E. Carroll, M. Green, A. M. R. Galas, M. Murray, T. W. Turney, A. J. Welch, and P. Woodward, J. Chem. Soc., Dalton Trans., 1980, 80.
 - 4) Y. Yamamoto and H. Yamazaki, J. Org. Chem., 42, 4136(1977).
 - 5) Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Jpn., 54, 787(1981).
 - 6) Y. Yamamoto and H. Yamazaki, Organometallics, 7, 2411(1988).
 - 7) Anal. Found: C, 81.81; H, 6.43; N, 7.24%. Calcd for $C_{26}H_{24}N_2O$: C, 82.08; H, 6.35; N, 7.36%.
 - 8) Crystal data: $C_{26}H_{24}N_2O$, $M = 380.49$, monoclinic, space group $C2/c$, $a = 28.479(5)$, $b = 9.648(1)$, $c = 19.274(7)$ Å, $\beta = 123.74(3)^\circ$, $V = 4403.8(8)$ Å³, $Z = 8$, $D_c = 1.148$ g cm⁻³, monochromatied radiation (Mo K α). Reflection data with $2\theta < 52$ were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by block-diagonal least-squares techniques to $R = 0.061$ and $R_w = 0.059$, using 1846 unique reflections with $F_o > 5\sigma(F_o)$. The calculations were carried out with Universal Computation Program System UNICS III (T. Sakurai and K. Kobayashi, Rikagaku Kenkyusho Hokoku, 55, 69(1979)).
 - 9) 2b: ¹H NMR (CDCl₃): δ 2.15 and 2.25 (s, o-Me), 2.37 (s, p-Me), 5.89 (s, C=CH); IR (nujol) 1744(sh), 1708, 1670(sh), 1607(sh), 1595, 1562 cm⁻¹; Anal. Found: C, 82.09; H, 6.79; N, 7.05%. Calcd for $C_{27}H_{26}N_2O$: C, 82.20; H, 6.64; N, 7.10%. 2c: ¹H NMR (CDCl₃): δ 2.15 and 2.25 (s, o-Me), 3.83 (s, p-MeO), 5.81 (s, C=CH); IR (nujol) 1718, 1601(sh), 1579, 1559(sh), 1503 cm⁻¹; Anal. Found: C, 78.95; H, 6.47; N, 6.96%. Calcd for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82%. 2d: ¹H NMR (CDCl₃): δ 2.17 and 2.27 (s, o-Me), 5.98 (s, C=CH); IR (nujol) 1716, 1642, 1601(sh), 1588, 1557(sh), 1515 cm⁻¹; Anal. Found: C, 82.60; H, 6.15; N, 6.01%. Calcd for $C_{32}H_{28}N_2O$: C, 84.17; H, 6.18; N, 6.14%. 2e: ¹H NMR (CDCl₃): δ 2.13 and 2.27 (s, o-Me), 6.14 (s, C=CH); IR(nujol) 1712, 1682, 1606, 1584, 1526 cm⁻¹; Anal. Found: C, 72.76; H, 5.48; N, 9.70%. Calcd for $C_{26}H_{23}N_3O_3$: C, 73.39; H, 5.45; N, 9.88%.
 - 10) HPLC analysis was performed with TSK-CCPM system (TOSOH Co. Ltd.) using a ODS-80TM column.

(Received March 2, 1991)