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Cobalt-catalyzed Preparation of Diiminofuran Derivatives through Double Insertion of Isocyanide into a Metal-Carbon Bond[1)]

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The reaction of 2-bromoacetophenone with XylNC (Xyl = 2,6-xylyl) in the presence of Et_3N and cobalt complex such as $Co_2(XylNC)_8$, $CoBr_2(XylNC)_4$, $[Co(XylNC)_5](PF_6)$ 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 $Co_2(CO)_8$, 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 $Co_2(RNC)_8$ 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 $Co_2(XylNC)_8$ was refluxed in toluene. After 6 h, the deep red solution was chromatographed on alumina to give reddish orange crystals formulated as $(XylNC)_2(C_6H_5COCH)$ (2a) in a few yield.[7)] When this reaction was carried out in the presence of triethylamine, the reaction proceeded catalytically and formation of $[Et_3NH]Br$ 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 $Co_2(XylNC)_8$ (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, [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)°. 4'-Substituted 2-bromoacetophenone (**1b**: 4'-Me; **1c**: 4'-MeO, **1d**: 4'-Ph, **1e**: 4'-NO_2) also afforded 2,3-bis-N-(2',6'-xylyl)imino-5-(4'-R'-phenyl)-2,3-dihydrofuran (R' = **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).

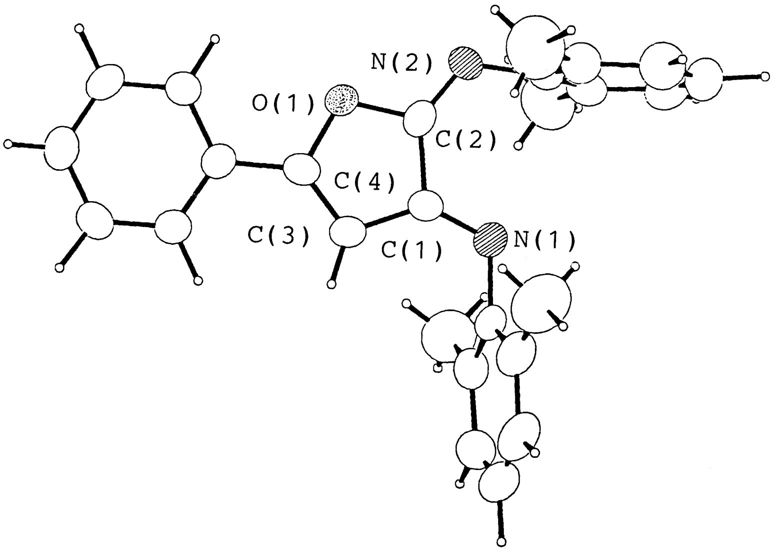
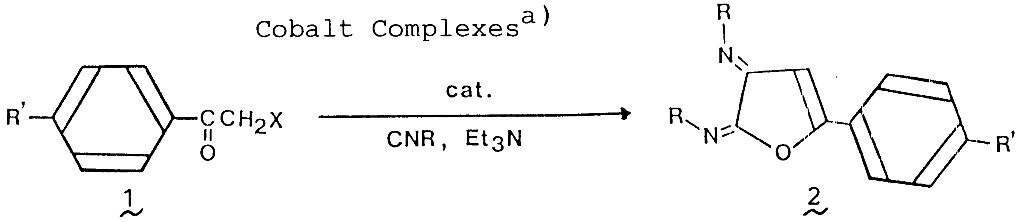


Fig. 1. An ORTEP drawing of **2a**. Selected bond distances (Å) and angles (deg); O(1)-C(2) 1.396(8), O(1)-C(4) 1.386(6), N(1)-C(1) 1.284(8), N(2)-C(2) 1.247(6), C(1)-C(2) 1.506(9), C(1)-C(3) 1.435(7), C(3)-C(4) 1.347(9), C(2)-O(1)-C(4) 107.4(5), C(2)-C(1)-C(3) 104.8(5), O(1)-C(2)-C(1) 106.8(4), C(1)-C(3)-C(4) 108.0(5), O(1)-C(4)-C(3) 113.0(5).

In an attempt to investigate the catalytic species, NH_4PF_6 was added to the solution after the catalytic reaction was over. $[Co(XylNC)_5](PF_6)$ was isolated in a good yield, suggesting the presence of a Co(I) species in the reaction. When $CoBr_2(XylNC)_4$ or $Co(acac)_3$ was treated with XylNC in the presence of Et_3N and NH_4PF_6, $[Co(XylNC)_5](PF_6)$ 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

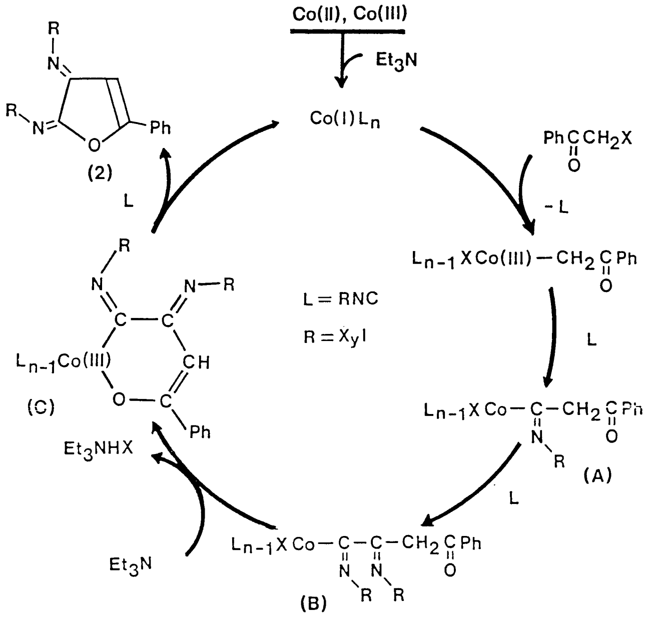
Table 1. Catalytic Formation of Diiminofurans Promoted by Cobalt Complexes[a)]



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	$CoBr(XylNC)_5$	H	2a	23	11.8
4	$Co(XylNC)_5PF_6$	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/Et_3N/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.

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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, β = 123.74(3)°, V = 4403.8(8) $Å^3$, Z = 8, D_c = 1.148 g cm^{-3}, monochromatied radiation (Mo $K\alpha$). 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 Rw = 0.059, using 1846 unique reflections with $Fo > 5\sigma(Fo)$. 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 ($CDCl_3$): 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 ($CDCl_3$): 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 ($CDCl_3$): 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 ($CDCl_3$): 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.

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