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Phenyl substitution reactions of 3-bromo-2,4-pentanedionato complexes

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Abstract

Phenyl substitution reactions of 3-bromo-2,4-pentanedionate metal (M = Cr and Co) complexes catalyzed by palladium (Suzuki coupling reaction) were carried out. Variously substituted products were identified by standard spectroscopic methods. In order to confirm the products, crystal structures of the several products were determined by the X-ray diffraction method. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Suzuki reaction; Catalysis; Chromium complexes; Cobalt complexes; Acetylacetonate complexes

1. Introduction

About 40 years ago, there was a heated discussion in the field of coordination chemistry that metal acetylacetonates ($M(acac)_n$, $n = 2$ or 3) might have an aromatic character on the basis of large stability constants [1]. In fact, many acetylacetonate complexes have remarkable stabilities and show various properties similar to aromatic compounds. Collman, Nyholm and Kluiber performed many electrophilic reactions on the γ-position of $M(acac)_3$ (M = Cr, Co, Rh) [2]. Although the eager hope for demonstrating the aromatic character of acetylacetonate rings has subsided recently, the work on the aromaticity of Collman and others attracted and encouraged us to investigate similar substitution reactions. Here, we report aryl substitution reactions (Suzuki coupling reaction [3]) of metal γ-bromoacetylacetonates. The Suzuki coupling reaction is one of the most important reactions due to its mild conditions and good results over a wide range of aryl halides and aryl oxysulfonates. Arylboronates for example give biaryls which can be prepared by Ullmann reaction in low yields only. The Suzuki reaction conditions are so mild that almost all functional groups are usually tolerated. We attempted a Pd(0) catalyzed cross coupling reaction of metal 3-bromo-2,4-pentanedionate with phenylboronic acid as shown in Fig. 1. In this paper, we describe the results of Suzuki coupling reactions on $M(acac)_3$ (M = Cr, Co).

2. Experimental

2.1. Materials and instruments

All reagents were obtained from chemical companies and used without purification. Bromination of $Cr(acac)_3$ and $Co(acac)_3$ were performed with NBS [4]. Using JEOL GSX-400, ^1H NMR and ^{13}C NMR were obtained. Infrared spectra (400–4000 cm^{-1}) and mass spectra were measured with a JASCO FT/IR-300E and JEOL DX-300, respectively. Since metal complexes are generally not so stable in severe conditions, mass spectral data of metal complexes under usual measurement conditions are useful only in limited cases. Most of the

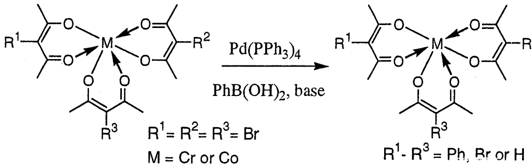

Fig. 1. Cross coupling reactions of $M(\gamma\text{-}X\text{-}acac)_3$.

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Table 1
Reaction products and yields

	M = Cr					M = Co			
	R^1	R^2	R^3	Yield (%)		R^1	R^2	R^3	Yield (%)
a	Ph	Br	Br	23 [a]	a	Br	Br	H	7
b	Ph	Ph	Br	3	b	Ph	Br	H	4
c	Ph	Br	H	7 [a]	c	Br	H	H	25
d	Ph	Ph	H	0.8	d	Ph	H	H	7 [a]

[a] The crystal structure of the product was determined by X-ray diffraction.

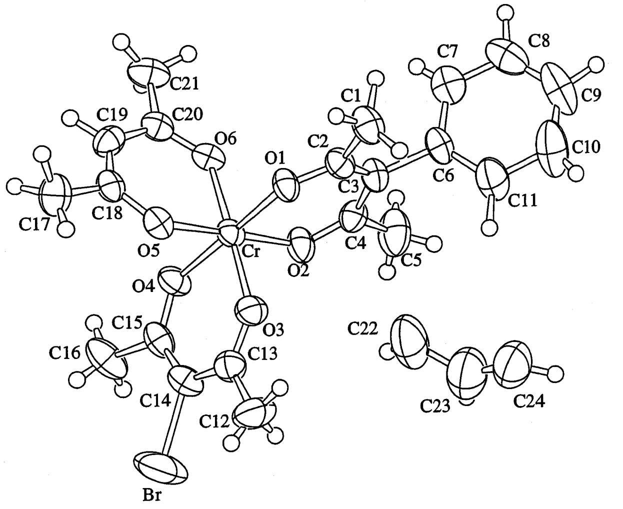


Fig. 2. ORTEP drawing of **Cr-c** showing atom labeling scheme. Carbon atoms, C(22)–C(24) are half of the solvated benzene.

chromium and cobalt complexes in this report are stable enough to show molecular ions. Elemental analyses were performed on a Yanaco MT-5.

2.2. Phenyl substitution reactions

A mixture of M(3-Br-acac)$_3$ (10 mmol), phenylboronic acid (33 mmol), finely powdered solid base (NaOH or Ba(OH)$_2$·6H$_2$O) (33 mmol), Pd(PPh$_3$)$_4$ (0.3 mmol), and benzene (50 ml) was refluxed for 24 h under argon. The reaction mixture was filtered once and washed with water, then dried with Na$_2$SO$_4$. The solvent was evaporated and the residue was subjected to chromatography. In the case of the chromium complex, biphenyl and many components of chromium complexes were discernible on TLC. In the case of chromium, five components were isolated as listed in Table 1 from **Cr-a** to **Cr-e**. Biphenyl and **Cr-a** components were eluted at the same time with a mixture of benzene and hexane (5:2), and the other components were eluted with a mixture of benzene and ethyl acetate (7:1). Since **Cr-b** was contaminated with several organic species after chromatography, the solid of **Cr-b** was washed with hexane and recrystallized from a mixture of hexane and benzene. All the components were eluted with benzene in the case of the cobalt complex.

2.3. Characterization of chromium and cobalt complexes

Cr-a (yield = 23%): m.p. 170 °C. *Anal.* Found: C, 43.2; H, 3.8. Calc. for $C_{21}H_{23}Br_2CrO_6$ (FW = 583.22): C, 43.3; H, 4.0%. IR (KBr) ν (cm^{-1}); 441 (w), 468 (s), 610 (m), 640 (m), 707 (s), 768 (s), 922 (s), 985 (m), 1025 (s), 1335 (s), 1421 (s), 1460 (s), 1556 (s), 3019 (w). MS: *m/e* 583, 585, 587, 406.

Cr-b (yield = 3%): m.p. 219 °C. *Anal.* Found: C, 56.0; H, 4.9. Calc. for $C_{27}H_{28}BrCrO_6$ (FW = 580.42): C, 55.9; H, 4.9%. IR (KBr); ν (cm^{-1}), 469 (m), 615 (w), 708 (m), 781 (w), 930 (m), 1341 (s), 1423 (s), 1448 (s), 1561 (s), 3023 (w). MS: *m/e* 581, 579, 402.

Cr-c (Fig. 2) (yield = 7%): m.p. 107 °C. *Anal.* Found: C, 56.0; H, 4.90. Calc. for $C_{21}H_{24}BrCrO_6$ (FW = 504.11): C, 55.9; H, 4.9%. IR (KBr); ν (cm^{-1}), 465 (m), 613 (w), 707 (w), 921 (w), 1021 (m), 1274 (m), 1339 (s), 1424 (s), 1560 (s) cm^{-1}. MS: *m/e* 503,505, 326.

Cr-d (yield = 0.8%): m.p. 198 °C. *Anal.* Found: C, 64.6; H, 5.8. Calc. for $C_{27}H_{29}CrO_6$ (FW = 501.53): C, 64.7; H, 5.4%. IR (KBr); ν (cm^{-1}), 483 (w), 632 (w), 930 (w), 1013 (w), 1367 (m), 1441 (m), 1525 (m), 1573 (s). MS: *m/e* 501, 402, 326, 151.

Cr-e (yield = 1.4%): $C_{15}H_{20}BrCrO_6$ (428.23): m.p. 193 °C. IR (KBr); ν (cm^{-1}), 460 (s), 596 (m), 624 (m), 708 (m), 772 (m), 929 (m), 1016 (s), 1279 (s), 1383 (s), 1425 (s), 1520 (s), 1573 (s). MS: *m/e* 429, 427, 326, 250, 151.

Co-a (yield = 7%): m.p. 147–149 °C. *Anal.* Found: C, 34.8; H, 3.6. Calc. for $C_{15}H_{19}Br_2CoO_6$ (FW = 514.04): C, 35.1; H, 3.7%. ^{1}H NMR (CDCl$_3$): δ 5.55 (H, s), 2.53 (6H, s), 2.49 (6H, s), and 2.21 (6H, s). ^{13}C NMR (CDCl$_3$): δ 189.80, 188.40, 96.70, 94.70, 29.74, 29.61, 25.98. IR (KBr); ν (cm^{-1}), 474 (s), 648 (m), 697 (w), 771 (w), 930 (w), 986 (m), 1028 (s), 1338 (s), 1362 (s), 1419 (s), 1460 (w), 1519 (s), 1551 (vs), 1637 (w), 3435 (s, br). MS: *m/e* 515, 513, 511, 334, 319, 158.

Co-b (yield = 4%): m.p. 125–128 °C. *Anal.* Found: C, 49.6; H, 4.7. Calc. for $C_{21}H_{24}BrCoO_6$ (FW = 511.25): C, 49.3; H, 4.7%. ^{1}H NMR (CDCl$_3$): δ 7.45–7.29 (5H), 5.57 (H, s), 2.56 (3H, s), 2.51 (3H, s), 2.23 (6H, s), 1.98 (3H, s), and 1.94 (3H, s). ^{13}C NMR (CDCl$_3$): δ 189.88, 189.49, 188.58, 188.39, 188.28, 188.09, 139.95, 131.92, 128.80, 128.34, 127.05, 112.00, 97.35, 95.00, 77.37, 77.05, 76.72, 29.74, 26.93, 26.77, 26.20, 26.06. IR (KBr); ν (cm^{-1}), 471 (s), 645 (m), 708 (m), 927 (w), 982 (w), 1025 (s), 1342 (vs), 1365 (s), 1421 (s), 1520 (s), 1556 (vs), 1628 (sh), 2912 (w), 3435 (m, br). MS: *m/e* 513, 511, 509, 333, 242, 158.

Co-c (yield = 25%): m.p. 149–151 °C. *Anal.* Found: C, 41.6; H, 4.4. Calc. for $C_{15}H_{20}BrCoO_6$ (FW = 435.16): C, 41.4; H, 4.6%. ^{1}H NMR (CDCl$_3$): δ 5.54

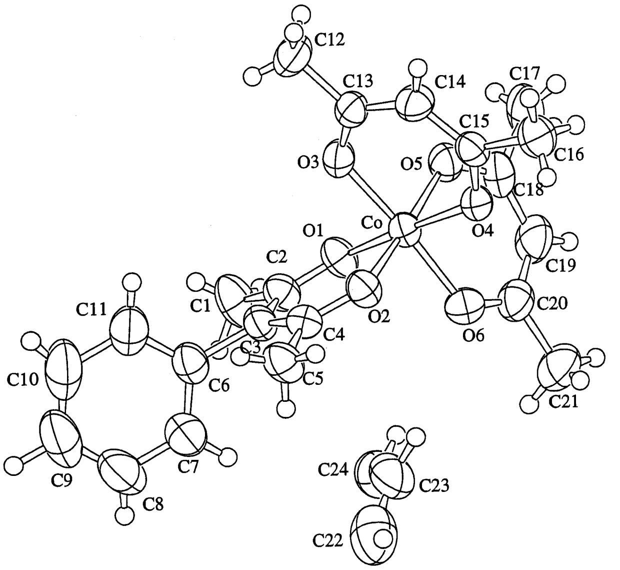


Fig. 3. ORTEP drawing of **Co-d** showing atom labeling scheme. Carbon atoms, C(22)–C(24) are half of the solvated benzene.

(2H, s), 2.50 (6H, s), 2.22 (6H, s), and 2.18 (6H, s). ^{13}C NMR ($CDCl_3$): δ 189.72, 189.56, 188.14, 97.15, 77.37, 77.05, 76.73, 29.71, 26.12, 25.98. IR (KBr); ν (cm^{-1}), 470 (s), 637 (m), 678 (m), 766 (m), 936 (w), 984 (m), 1027 (s), 1193 (w), 1281 (m), 1362 (vs), 1423 (s), 1519 (vs), 1556 (vs), 1637 (w), 2921 (w), 3005 (w), 3435 (s, br). MS: *m*/*e* 435,433, 334, 257, 158.

Co-d (Fig. 3) (yield = 7%): m.p. 165–166 °C. *Anal.* Found: C, 61.1; H, 6.2. Calc. for $C_{21}H_{25}CoO_6$ (FW = 432.36): C, 61.2; H, 6.0%. ^{1}H NMR ($CDCl_3$): δ 7.38–7.17 (5H), 5.56 (2H, s), 2.24 (6H, s), 2.20 (6H, s), and 1.94 (6H, s). ^{13}C NMR ($CDCl_3$): δ 189.63, 189.41, 188.33, 140.26, 131.98, 128.74, 126.90, 112.34, 97.29, 77.38, 77.05, 76.73, 26.83, 26.15. IR (KBr); ν (cm^{-1}), 474 (w), 633 (w), 707 (w), 771 (w), 930 (w), 1023 (w), 1388 (m), 1522 (s), 1571 (vs), 1637 (w), 3446 (s, br). MS: *m*/*e* 432, 333, 242, 158.

2.4. X-ray crystallography

Crystallographic data are listed in Table 2. Since two chloroform molecules were included in the complex of **Cr-a** and the crystals tend to deteriorate probably due to loss of part of them during the measurement, they had to be coated with a sticking agent. Reflection intensities of all the crystals were measured at room temperature with Rigaku AFC7R diffractometer. Intensity data were corrected for absorption. The structures were solved by direct methods (SIR92) [5] and

Table 2
Crystallographic data [a]

Complex	**Cr-a**	**Cr-c**	**Co-d**
Crystallizing solvent	$CHCl_3$	benzene–hexane	benzene–hexane
Formula	$C_{23}H_{25}Br_2CrO_6Cl_6$	$C_{24}H_{27}BrCrO_5$	$C_{24}H_{28}CoO_6$
Formula weight	821.97	543.47	471.41
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions			
a (Å)	12.849(7)	12.004(2)	11.702(2)
b (Å)	14.646(8)	14.413(3)	14.052(4)
c (Å)	17.458(7)	7.490(1)	7.478(1)
α (°)	90.0	101.46(1)	97.60(2)
β (°)	100.35(4)	92.79(1)	99.15(1)
γ (°)	90.0	102.25(2)	101.05(2)
V (Å^3)	3231(2)	1235.5(4)	1174.5(5)
Z	4	2	2
D_{calc} (g cm^{-3})	1.689	1.461	1.333
μ (cm^{-1})	33.64	21.20	7.66
$2\theta_{max}$	55.0	60.0	60.0
h	0 to 16	0 to 15	0 to 16
k	−22 to 22	−20 to 19	−19 to 19
l	−19 to 0	−10 to 10	−10 to 10
Crystal size (mm)	0.63 × 0.56 × 0.53	0.50 × 0.20 × 0.13	0.53 × 0.50 × 0.25
Total reflections	7766	6172	8031
Unique reflections	7435	5851	7694
Reflections observed [$I > 2.0\sigma(I)$]	3527	2477	3898
R [b]	0.057	0.058	0.041
Rw [c] (p-factor)	0.070(0.04)	0.071(0.036)	0.041(0.019)
Goodness-of-fit	1.81	1.75	1.67

[a] Radiation: Mo Kα (graphite monochromated, $\lambda = 0.71069$).

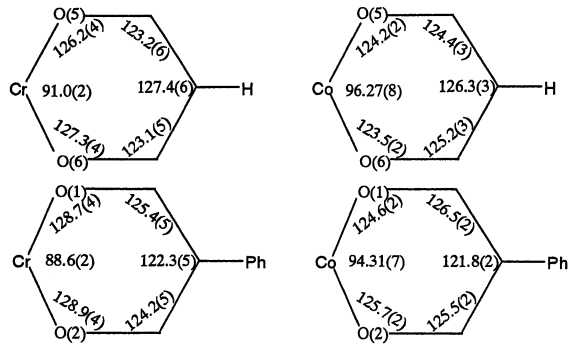
[b] $R = (||F_o| - |F_c||/\Sigma|F_o|)$.

[c] $Rw = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = [\sigma_c^2(F_o) + p^2/4)F_o^2]^{-1}$, p = p-factor.

Table 3
Selected bond distances (Å) and angles (°)

complex coordination bonds	**Cr-a**	**Cr-c**	**Co-d**
M-O(1)	1.936(4)	1.952(4)	1.878(2)
M-O(2)	1.933(4)	1.941(4)	1.880(2)
M-O(3)	1.952(4)	1.952(4)	1.879(2)
M-O(4)	1.945(4)	1.957(4)	1.890(2)
M-O(5)	1.951(4)	1.964(4)	1.890(2)
M-O(6)	1.949(4)	1.946(4)	1.888(2)
C-O(1)	1.278(7)	1.276(7)	1.278(3)
C-O(2)	1.280(7)	1.287(7)	1.269(3)
C-O(3)	1.272(7)	1.263(7)	1.264(3)
C-O(4)	1.283(7)	1.286(7)	1.257(3)
C-O(5)	1.274(7)	1.290(7)	1.262(3)
C-O(6)	1.266(7)	1.270(7)	1.261(3)

Important bond angles of Cr-c and Co-d complexes are shown below.



structure refinement were performed with full-matrix least-squares. All the calculations were performed using TEXSAN program system on the SGI Indy computer at the Center for Instrumental Analysis of Ibaraki University.

3. Results and discussion

Palladium-catalyzed cross coupling reactions of metal (Cr(III) and Co(III)) γ-haloacetylacetonates with phenylboronic acid gave a complex mixture of variously phenyl-substituted metal complexes and reduced products (see Table 1). After standard open column chromatography was repeated twice, the crude products were recrystallized from the appropriate solvents (indicated in Table 2). Chromium complexes were isolated more easily than cobalt complexes, probably due to the inertness of chromium complexes under the hydrolytic conditions. Chromium complexes were identified by IR, mass spectrometry and elemental analyses, and finally by X-ray diffraction method. In the case of cobalt complexes, NMR spectroscopy was also useful to identify the structures. Infrared spectral features assigned to C=O and C=C of the acac ring in the region of 1500–1600 cm^{-1} were observed according to 0–3 substitution pattern. Those strong peaks characteristic of β-diketone complexes were underlined in Section 2.3. Substituted chelate rings and non-substituted rings showed strong peaks at 1550–1570 and 1515–1530 cm^{-1}, respectively.

In all the reactions, large amounts of biphenyl and various materials reduced to non-substituted chelate rings were isolated. The formation of biphenyl has been explained previously [6]. Since it is formed from intermediate ionic borate species, its formation was assumed to be inevitable in our experiments and biphenyl was isolated in varying yields (17–48%). Low yields of phenyl-substituted products in all the reactions might be attributable to steric hindrance at the reaction center. In the case of iodoacetylacetonatochromium complex, only a trace (0.4%) of Cr(acac)$_2$(Phacac) was obtained, while a large amount of Cr(acac)$_3$ (35%) was isolated. In the case of chloroacetylacetonatochromium complex, none of the phenyl-substituted complex was isolated except biphenyl which was probably formed from phenylboronic acid.

Other electrophilic substitution reactions have to be attempted and will be reported elsewhere.

4. Description of the structure

Crystal structures of the two chromium complexes and the cobalt complex were determined. The crystallographic data are summarized in Table 2. In the case of the **Cr-a**, one of two chloroform molecules included in the unit cell has a disordered structure and large thermal parameters. In the case of **Cr-c** and **Co-d,** both complexes have one molecule of benzene per unit cell. ORTEP drawings of **Cr-c** and **Co-d** were shown in Figure 2 and Figure 3, respectively. The phenyl rings introduced in this reaction have an almost perpendicular orientation against the acac ring. Selected bond distances and angles of **Cr-c** and **Co-d** are listed in Table 3. Coordination bonds (M–O) of chromium complexes are in the range of 1.931–1.978 Å and those of cobalt complexes are 1.878–1.891 Å. The coordination bonds in the cobalt complex are rather short compared to those of chromium complexes. This fact can be ascribed to the smaller effective nuclear charge of the cobalt atom compared to that of the chromium atom.

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