Journal of Organometallic Chemistry, 359 (1989) C57–C60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

The reaction of *N*-phenyldialkynylimines with η^5-cyclopentadienyldicarbonylcobalt

Yoshihiko Ito *, **Masahiko Inouye, Masahiro Murakami**
Department of Synthetic Chemistry, Kyoto University, Kyoto 606 (Japan)

and Motoo Shiro
Shionogi Research Laboratories, Fukushima-ku, Osaka 553 (Japan)

(Received September 9th, 1988)

Abstract

N-Substituted dialkynylimines react with η^5-cyclopentadienyldicarbonylcobalt to give a mixture of η^4-cyclobutadiene cobalt complexes, the structures of which have been determined by X-ray crystallography.

Cobalt-mediated cyclo-oligomerizations of alkynes have been intensively studied [1], and have been developed into a versatile synthetic method [2]. In addition, the reactions of alkynes with cobalt(I) complexes such as $Co(CO)_2Cp$ and $Co(PPh_3)_2Cp$ have often given the corresponding η^4-cyclobutadiene cobalt complexes [3]. Here we report the reaction of *N*-substituted dialkynylimines with η^5-cyclopentadienyldicarbonylcobalt to give a mixture of η^4-cyclobutadiene cobalt complexes (**3**, **5** and **6**), the structures of which have been determined by X-ray crystallography.

Unlike dialkynyl ketones which are thermally less stable, *N*-phenyldialkynylimines could be subjected to reaction with η^5-cyclopentadienyldicarbonylcobalt at high temperature (ca. 165 °C) to form a new type of η^4-cyclobutadienecobalt complex. To a solution of *N*-phenyldialkynylimine (**1**, 1.0 mmol), which was prepared by palladium-catalyzed coupling of *N*-phenyl isocyanide dichloride with an alkynyltin compound [4], in mesitylene (3 ml), was added $Cp(CO)_2Co$ (1.0 mmol) in mesitylene (15 ml) during ca. 1 h at 165 °C. After 30 min stirring at that temperature, the solvent was removed in vacuo and the residue was subjected to TLC on silica gel (n-hexane : ether = 20 : 1) to give the η^4-cyclobutadiene cobalt complexes (**3**, **5** and **6**) as shown in Scheme 1. Dialkynylimines (**1c** and **1d**) give only η^4-cyclobutadienecobalt complexes (**3c** and **3d**, respectively). However, the dialkynylimines (**1a** and **1b**) give not only **3a** and **3b**, but also the bis(cyclopentadienylcobalt) complexes (**5a** and **5b**), which are marked by a novel structure of dietheno-*p*-benzoquinone diimine [**5a**: m.p. > 290 °C; IR (KBr) 1584 (C=N) cm^{-1}; ^{1}H NMR

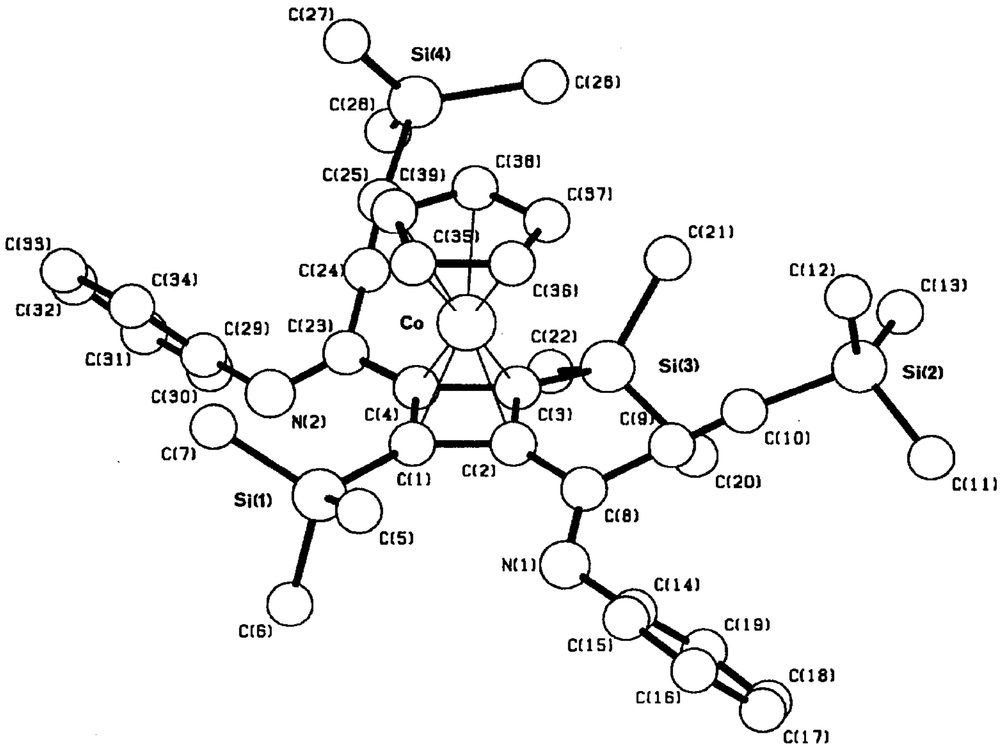


Fig. 1. Structure of **3a**. Selected bond lengths (Å) and angles (°): Co–Y 1.674(1), Co–Z 1.666(2), C(1)–C(2) 1.46(1), C(2)–C(3) 1.50(1), C(3)–C(4) 1.46(1), C(1)–C(4) 1.48(1), Y–Co–Z 178.3(5). Co–Y = vertical line from Co to mean plane of cyclobutadiene ring. Co–Z = vertical line from Co to mean plane of cyclopentadiene ring.

($CDCl_3$) δ 0.09 (s, 36H), 4.77 (s, 10H), 6.91–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 1.67, 81.53, 119.82, 122.72, 129.69, 151.91, 160.18; UV (CH_2Cl_2) λ_{max} 425 (ϵ = 11900), 305 (31300), 249 (43200) nm; MS (20 eV) m/z 842 (M^+). Anal. Found: C, 62.72; H, 6.72; N, 3.44. $C_{44}H_{56}N_2Si_4Co_2$ calcd.: C, 62.68; H, 6.69; N, 3.32%. **5b**: m.p. > 290 °C; IR (KBr) 1582 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.11 (s, 10H), 6.63–7.87 m, 30H); ^{13}C NMR ($CDCl_3$) δ 164.52 (C=N); FD-MS, m/z 858 (M^+)].

The structures of **3a** * and **5a** have been determined by X-ray crystallography **

---

* Physical and spectral data. *For 3a*: m.p. 189–191 °C; IR (KBr): 2270 (C≡C), 1558 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$, cyclohexane as internal standard): δ 0.13 (s, 18H), 0.39 (s, 18H), 5.00 (s, 5H), 6.85–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$): δ −0.70, 1.62, 72.35, 81.87, 86.12, 99.65, 102.74, 120.44, 124.34, 128.21, 150.29, 151.63; UV (CH_2Cl_2): λ_{max} 347 (ϵ = 19300), 294 (26200), 248 (29000) nm; MS (24 eV): m/z 718 (M^+). Anal. Found: C, 65.13; H, 7.11; N, 3.92. $C_{35}H_{51}N_2Si_4Co$ calcd.: C, 65.14; H, 7.15; N, 3.90%. *For 6a*: m.p. 259–261 °C; IR (KBr): 1576 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.09 (s, 36H), 5.20 (s, 10H), 6.90–7.56 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 1.98, 81.04, 121.81, 123.07, 129.21, 151.49, 161.28; MS (20 eV): m/z 842 (M^+).

** *Crystal data for 3a*: $C_{39}H_{51}N_2Si_4Co$, M = 719.1, triclinic, space group $P\bar{1}$, a 13.058(4), b 15.058(4), c 12.541(5) Å, α 101.40(3), β 116.85(3), γ 86.42(3)°, U 2156(1) $Å^3$, D_c 1.108 g cm^{-3} for $Z = 2$, $F(000) = 764$, λ(Mo-K_α) 0.71069 Å, μ 5.49 cm^{-1}, T 25 °C, crystal size 0.3 × 0.3 × 0.3 mm. *For 5a*: $C_{44}H_{56}N_2Si_4Co_2$, M = 843.2, tetragonal, space group $I4_1/a$, a 24.726(6), c 14.554(5) Å, U 8898(4) $Å^3$, D_c 1.259 g cm^{-3} for $Z = 8$, $F(000) = 3552$, λ(Mo-K_α) 0.71069 Å, μ 9.12 cm^{-1}, T 25 °C, crystal size 0.4 × 0.4 × 0.4 mm.

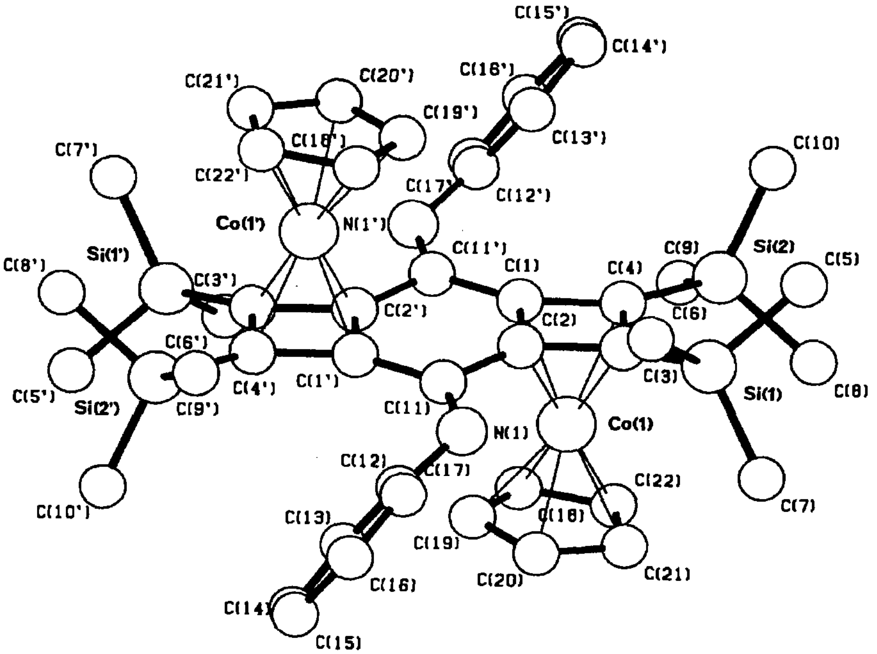
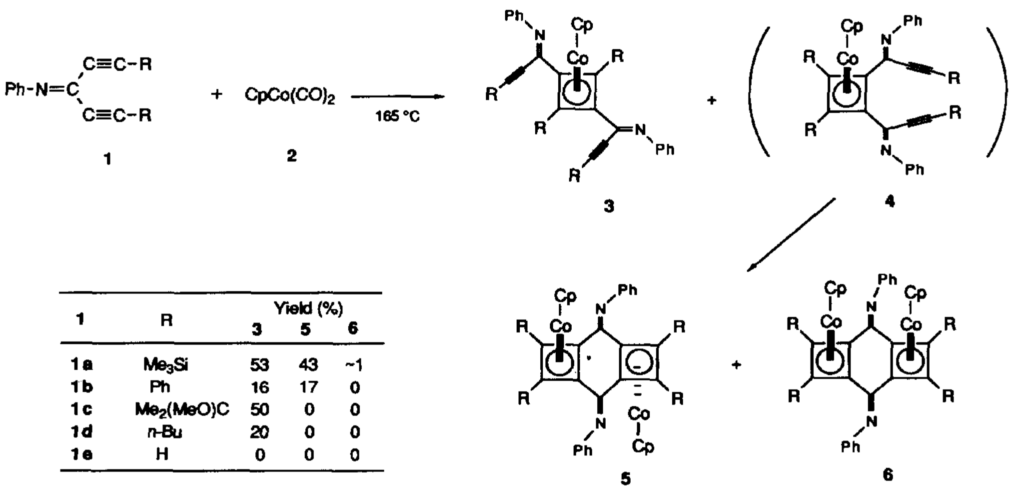


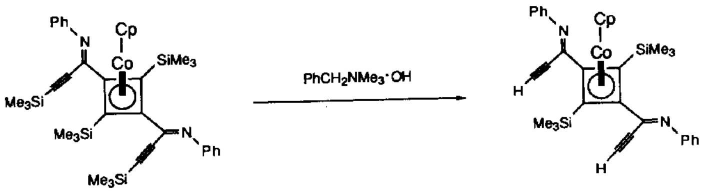
Fig. 2. Structure of **5a**. The two halves of the molecule are related by an inversion center in the crystal, so that symmetry-related atoms in one of a pair are primed in the other. Selected bond lengths (Å) and angles (°): Co(1)–Y(1) 1.692(1), Co(1)–Z(18) 1.692(2), C(1)–C(2) 1.459(4), C(2)–C(3) 1.473(4), C(3)–C(4) 1.504(4), C(1)–C(4) 1.484(4), Y(1)–Co(1)–Z(18) 174.0(2). Co(1)–Y(1) = vertical line from Co(1) to mean plane of cyclobutadiene ring containing C(1). Co(1)–Z(18) = vertical line from Co(1) to mean plane of cyclopentadiene ring containing C(18).

and are shown in Figures 1 and 2, together with selected bond lengths and angles. The structure of **6a** *, which was not interconvertible to **5a**, was deduced on the basis of ^1H NMR, ^{13}C NMR, IR, and MS data, which are similar to those for **5a**.



1	R	Yield (%)		
		3	5	6
1a	Me$_3$Si	53	43	~1
1b	Ph	16	17	0
1c	Me$_2$(MeO)C	50	0	0
1d	n-Bu	20	0	0
1e	H	0	0	0

Scheme 1



3a **7**

Scheme 2

The present reaction of **1a** with **2** may be explained in terms of competitive head-to-tail and head-to-head cyclodimerizations of **1a** to produce, respectively, **3a** and **4a**, with **4a** undergoing further intramolecular cyclization to give **5a** and **6a**.

While *N*-phenyldiethynylimine (**1e**, R = H) is thermally unstable and gives only a tarry substance after reaction with **2**, **3a** was readily protodesilylated to afford **7** in a high yield (98%), after treatment with *N*-benzyltrimethylammonium hydroxide (Scheme 2).

Attempts to hydrolyze the imino group of the η^4-cyclobutadiene cobalt complexes (**3** and **5**) to the corresponding carbonyl group have been unsuccessful.

The intensity data, 6357 independent reflections for **3a** and 3289 for **5a**, were collected on a Rigaku AFC-5R diffractometer in the region of $0.2 \le 2\theta \le 47°$ using an ω–2θ scan technique ($\Delta\omega = A + 0.5 \tan\theta$, $A = 1.4°$ for **3a** and 0.8° for **5a**). Absorption corrections for the spherical crystals were approximate, transmission factors being constant in the range of 2θ, viz., 0.885 for **3a** and 0.847 for **5a**. The structures were solved by the heavy atom method; H atoms, except those in the methyl groups, were located from difference electron density maps. The positional parameters for all the atoms and the anisotropic thermal parameters for the non-H atoms were refined by the block-diagonal least squares. Temperature factors for each H atom were taken to be equal to B_{eq} of the atom to which it is bonded. Atomic scattering factors were calculated by the analytical form [5]. No anomalous dispersion corrections were applied because of the small f' and f'' values for Co and Si. Final R, R_w and S values were respectively 0.088, 0.127 and 1.199 for **3a**, and 0.043, 0.055 and 1.082 for **5a**. Weights were taken as $w = [\sigma^2(F_0) + c^2 | F_0 |^2]^{-1}$ ($c^2 = 0.00761$ for **3a** and 0.00146 for **5a**) for the reflections with $w^{1/2} | F_0 | > 3$ and $w^{1/2} | \Delta F | < 4$, and otherwise $w = 0$. 4012 reflections were used for the least-squares refinement for **3a**, and 2637 for **5a**. $\Delta\rho_{max}$ and $(\Delta/\sigma)_{max}$ were 0.7 e Å^{-3} and 0.4 for **3a**, and 0.5 e Å^{-3} and 0.2 for **5a**, respectively. The large R-value for **3a** may be due to the poor quality of the crystal. Tables of atomic co-ordinates and thermal parameters, and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

References

1 K. Yasufuku, A. Hamada, K. Aoki and H. Yamazaki, J. Am. Chem. Soc., 102 (1980) 4363.
2 K.P.C. Vollhardt, Acc. Chem. Res., 10 (1977) 1.
3 A. Efraty, Chem. Rev., 77 (1977) 691.
4 Y. Ito, M. Inouye and M. Murakami, Tetrahedron Lett., in press.
5 International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974, p. 99.