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# Synthesis and non-linear optical properties of (alkyne)dicobalt octacarbonyl complexes and their substitution derivatives

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# Abstract

A series of new donor-acceptor compounds of the form  $[(HC=C-CH=CH-C_6H_4-X_7)Co_2(CO)_4(L^1)(L^2)])]$  (2, X = Br, L<sup>1</sup> = L<sup>2</sup> = CO; 3, X = NO<sub>2</sub>, L<sup>1</sup> = L<sup>2</sup> = CO; 6, X = NO<sub>2</sub>, L<sup>1</sup> = CO, L<sup>2</sup> = PPh<sub>3</sub>; 7, X = NO<sub>2</sub>, L<sup>1</sup> = L<sup>2</sup> = PPh<sub>3</sub>; 8, X = NO<sub>2</sub>, L<sup>1</sup> = AsPh<sub>3</sub>, L<sup>2</sup> = PPh<sub>3</sub>), where X is a  $\pi$ -acceptor group and the (alkyne)Co<sub>2</sub>(CO)<sub>4</sub>(L<sup>1</sup>)(L<sup>2</sup>) moiety is a donor, has been synthesized. The different  $\sigma$ -donor/ $\pi$ -acceptor abilities of the ligands L<sup>1</sup> and L<sup>2</sup> allow tuning of the electronic and optical properties of complexes 2, 3 and 6–8: the hyperpolarizability values increase in the order 2 < 3 < 6 < 7 < 8. Density functional calculations reveal that the absolute values of  $\beta$  do not agree with experimental results, but the general trends are consistent with experiments. The X-ray crystal structures of 2, 6, and 7 are reported.

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# 1. Introduction

Molecular materials that exhibit non-linear optical properties are of great interest for potential applications in optical data processing technology. A wide variety of organic compounds have been shown to exhibit such properties and, more recently, organometallic compounds have been found to exhibit significant effects [1].

Metals can have a large diversity of coordination mode with various organic ligands and changing a ligand in the coordination sphere can affect the function of the metal fragment. For organometallic compounds, it is particularly easy to finely tune either the electronic and/or steric effect by substitution of labile ligands 1b[2]. For example, Müller's and Tamm's groups reported the facile tuning of the electronic and optical properties of transition metal  $\pi$ -arene tricarbonyl complexes by carbonyl substitution [2a,2b].

Alkynes can be complexed with transition metal metals through the  $\sigma$ - or  $\pi$ -bond. Recently,  $\sigma$ -acetylide

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and  $\sigma$ -enynyl metal complexes (M = Ru, Ni, Au) have attracted much attention as promising candidates for NLO materials [3]. However, to our knowledge, little study has been conducted on  $\pi$ -alkyne transition metal complexes. It is a general feature of  $\pi$ -alkyne complexes that electrons are back-donated from a metal d-orbital into the ligand LUMO [4]. Thus, it is expected that an electron-rich  $\pi$ -alkyne complex having (an) electronwithdrawing group(s) on the alkyne can behave like a push-pull NLO molecule. Furthermore, increasing the electron-withdrawing ability enhances the stability of alkyne complexes.

We have prepared dicobalt carbonyl complexes of alkyne with an electron-withdrawing group and examine their non-linear optical properties. These complexes offer the possibility of a new class of NLO chromophore with tuning of their optical properties by carbonyl substitution. Herein we report the synthesis and non-linear optical study of new alkyne dicobalt complexes. Recently, the semiempirical calculations of the NLO properties of  $[Co_2\{\mu-\eta^2-(C_6H_5)CC(C_6H_4NO_2)\}(CO)_6]$  have been published [5].

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# 2. Experimental

#### 2.1. General considerations

All reactions with air- or moisture-sensitive materials were carried out under nitrogen using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained with a Bruker 300 or 500 spectrometer. Elemental analyses were carried out at the National Center for Inter-University Research Facilities, Seoul National University. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. UV–Vis electronic absorption spectra were recorded on a Unikon 930 spectrophotometer. Compounds **1**, **9a**, and **9b** were previously reported [6].

#### 2.1.1. Synthesis of 2

To 30 ml of THF solution of (4-bromobenzyl)triphenylphosphonium bromide (0.37 g, 0.71 mmol) and 18crown-6 (a catalytic amount), KotBu (0.09 g, 0.77 mmol) was added. After the solution was stirred for 1 h, 1 (0.20 g, 0.59 mmol) was added to the solution. The resulting solution was stirred for 3 h at room temperature (r.t.). Excess water (50 ml) and Et<sub>2</sub>O (50 ml) was added to quench the solution. The etheral layer was collected and evaporated to dryness. Compounds 2 and 2-1 were separated by chromatography on a silica gel column eluting with C<sub>6</sub>H<sub>14</sub>. Compound 2: Yield: 34% (0.10 g, 0.20 mmol); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.47 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 15.3 Hz, 1H), 6.87 (d, J = 15.3 Hz, 1H), 6.28 (s, 1H) ppm; IR (KBr):  $v_{CO}$  2093 (s), 2026 (s), 2000 (s) cm<sup>-1</sup>. Anal. Found: C, 38.68; H, 1.26. Calc. for C<sub>16</sub>H<sub>7</sub>BrCo<sub>2</sub>O<sub>6</sub>: C, 38.98; H, 1.43%. Compound 2-1: Yield: 34%; <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta$  7.50 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 11.3 Hz, 1H), 6.59 (d, J = 11.3 Hz, 1H), 5.98 (s, 1H) ppm; IR (KBr):  $v_{CO}$  2093 (s), 2053 (s), 2022 (s) cm<sup>-1</sup>. Anal. Found: C, 38.77; H, 1.69. Calc. for C<sub>16</sub>H<sub>7</sub>BrCo<sub>2</sub>O<sub>6</sub>: C, 38.98; H, 1.43%.

## 2.1.2. Synthesis of 3

The same procedure as for the syntheses of **2** and **2-1** was applied except for the use of (4-nitrobenzyl)triphenylphosphonium bromide instead of (4-bromobenzyl)triphenylphosphium bromide. *trans*- and *cis*-Isomers were separated by chromatography on a silica gel column eluting with C<sub>6</sub>H<sub>14</sub> and Et<sub>2</sub>O (v/v, 5:1). Compound **3**: Yield: 37%; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.20 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.40 (d, J =15.3 Hz, 1H), 6.95 (d, J = 15.3 Hz, 1H), 6.32 (s, 1H) ppm; IR (KBr):  $v_{CO}$  2093 (s), 2055 (s), 2022 (s), 2000 (s), 1961 (s) cm<sup>-1</sup>. *Anal*. Found: C, 41.71; H, 1.68; N, 3.05%. Calc. for C<sub>16</sub>H<sub>7</sub>Co<sub>2</sub>NO<sub>8</sub>: C, 41.86; H, 1.54; N, 3.05%. Compound **3-1**: Yield: 37%; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.24 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 11.4 Hz, 1H), 6.69 (d, J = 11.4 Hz, 1H), 5.97 (s, 1H) ppm; IR (KBr):  $v_{CO}$  2094 (s), 2054 (s), 2025 (s), 1999 (s) cm<sup>-1</sup>.

#### 2.1.3. Synthesis of 4

Compound 1 (0.20 g, 0.59 mmol), PPh<sub>3</sub> (0.16 g, 0.59 mmol), and 30 ml of THF were added to a Schlenk flask. The reaction mixture was heated at reflux under N<sub>2</sub> for 3 h. After the solution was cooled to r.t., any solids were filtered off and the filtrate was evaporated to dryness. The crude product was purified by chromatography on a silica gel column eluting with C<sub>6</sub>H<sub>14</sub> and Et<sub>2</sub>O (v/v, 3:1). Removal of the solvent by a rotary evaporator and keeping in vacuo for a day gave brown solids in 68% yield (0.23 g, 0.40 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.58 (s, 1H), 7.43 (br s, 15H), 5.50 (br s, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  51.12 ppm; IR (KBr):  $v_{CO}$  2071 (s), 2014 (s), 1976 (s), 1652 (s) cm<sup>-1</sup>. *Anal*. Found: C, 54.08; H, 2.95. Calc. for C<sub>26</sub>H<sub>17</sub>Co<sub>2</sub>O<sub>6</sub>P: C, 54.38; H, 2.98%.

### 2.1.4. Synthesis of 4\*

To the solution of **9**\* (2.80 g, 3.4 mmol) in 20 ml of Et<sub>2</sub>O was added HBF<sub>4</sub>·OMe<sub>2</sub> (0.86 ml) at 0 °C. The solution was allowed to warm to r.t. and stirred for 1 h. Solvent was removed by cannular transfer. THF (20 ml) and saturated aq. Na<sub>2</sub>CO<sub>3</sub> solution (20 ml) were added to the residue. The THF layer was treated with CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and NH<sub>4</sub>Cl solution (20 ml). The CH<sub>2</sub>Cl<sub>2</sub> layer was collected and chromatographed on a silica gel eluting with  $C_6H_{14}$  and  $Et_2O$  (v/v, 10:1). Removal of the solvent gave 10\* in 63% yield. To the activated DMSO (0.45 ml of DMSO and 1.26 ml of oxalyl chloride) in 20 ml of CH<sub>2</sub>Cl<sub>2</sub> was added 10\* at -78 °C. After the solution was stirred for 15 min at -78 °C, Et<sub>3</sub>N (5 ml) was added. The resulting solution was allowed to warm to r.t. for 40 min. To the solution were added CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and NH<sub>4</sub>Cl solution (20 ml). The CH<sub>2</sub>Cl<sub>2</sub> layer was chromatographed on a silica gel column eluting with  $C_6H_{14}$  and  $Et_2O$  (5:1). Removal of the solvent gave 4\* in 28% yield (0.40 g). Compound **10\***: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.49–7.26 (m, 15H), 5.21 (d, J = 3.6 Hz, 1H), 4.18 (dd, J = 4.7, 14.2 Hz, 1H), 3.89 (dd, J = 7.4, 14.3 Hz, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$ 53.83 ppm; IR (KBr):  $v_{CO}$  2059 (s), 2005 (s) cm<sup>-1</sup>. Anal. Found: C, 53.82; H, 3.50. Calc. for C<sub>26</sub>H<sub>17</sub>Co<sub>2</sub>O<sub>6</sub>P: C, 54.19; H, 3.32%.

#### 2.1.5. Synthesis of 5

Compound 1 (0.20 g, 0.59 mmol), PPh<sub>3</sub> (0.48 g, 1.77 mmol), and 30 ml of THF were added to a Schlenk flask. The solution was heated at reflux under N<sub>2</sub> for 3 h. After the solution was cooled to r.t., any solids were filtered off and the filtrate was evaporated to dryness. The crude product was purified by chromatography on a silica gel column eluting with  $C_6H_{14}$  and  $Et_2O$  (v/v,

3:1). Removal of the solvent gave brown solids in 85% yield (0.41 g, 0.50 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.08 (s, 1H), 7.38 (m, 30H), 4.61 (t, *J* = 3.0 Hz, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  49.46 ppm; IR (KBr): *v*<sub>CO</sub> 2026 (br s), 1971 (s), 1644 (s) cm<sup>-1</sup>. *Anal*. Found: C, 63.58; H, 4.20. Calc. for C<sub>43</sub>H<sub>32</sub>Co<sub>2</sub>O<sub>5</sub>P<sub>2</sub>: C, 63.88; H, 3.99%.

# 2.1.6. Synthesis of 6

The same procedure as for the synthesis of **2** was applied except using **4** instead of **1**. Yield: 76%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.11 (d, J = 8.8 Hz, 2H), 7.37 (m, 15H), 7.23 (d, J = 8.9 Hz, 2H), 6.68 (d, J = 15.3 Hz, 1H), 6.36 (d, J = 15.4 Hz, 1H), 5.47 (d, J = 3.3 Hz, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  53.15 ppm; IR (KBr):  $v_{CO}$  2061 (br s), 2010 (s), 1961 (s) cm<sup>-1</sup>. *Anal*. Found: C, 57.05; H, 3.18; N, 1.92. Calc. for C<sub>34</sub>H<sub>32</sub>Co<sub>2</sub>NO<sub>8</sub>P: C, 57.16; H, 3.20; N, 2.02%.

# 2.1.7. Synthesis of 6\*

Ylide (0.50 g, 1.0 mmol) and t-BuOK (0.13 g, 1.4 mmol) in 10 ml of THF were stirred with a catalytic amount of 18-crown-6 for 1 h. Compound **4**\* (0.40 g, 0.70 mmol) was added to the solution. After the resulting solution was stirred for 5 h, excess  $CH_2Cl_2$  (50 ml) and saturated aq. NaCl solution (50 ml) were added. The  $CH_2Cl_2$  layer was chromatographed on a silica gel column eluting with  $C_6H_{14}$  and  $Et_2O$  (5:1). Removal of the solvent gave **6**\* in 82% yield (0.40 g).

#### 2.1.8. Synthesis of 7

The same procedure as for the synthesis of **6** was applied using excess PPh<sub>3</sub>. Yield: 91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.99 (d, J = 8.9 Hz, 2H), 7.36 (m, 30H), 6.81 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 15.2 Hz, 1H), 5.24 (d, J = 15.2 Hz, 1H), 4.60 (br s, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  52.07 ppm; IR (KBr):  $v_{CO}$  2014 (s), 1966 (s), 1953 (s), 1925 (s) cm<sup>-1</sup>. *Anal*. Found: C, 64.34; H, 4.08; N, 1.36. Calc. for C<sub>50</sub>H<sub>37</sub>Co<sub>2</sub>NO<sub>6</sub>P<sub>2</sub>: C, 57.16; H, 3.20; N, 2.02%.

# 2.1.9. Synthesis of 8

The same procedure as for the synthesis of 7 was applied except for the use of AsPh<sub>3</sub> instead of PPh<sub>3</sub>. Yield: 45%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.89 (d, J = 9.0 Hz, 2H), 7.30 (m, 30H), 6.71 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 15.5 Hz, 1H), 5.19 (d, J = 15.5 Hz, 1H), 4.53 (br s, 1H) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  52.36 ppm; IR (KBr):  $v_{\rm CO}$  2061 (s), 2015 (s), 1953 (s), 1926 (s) cm<sup>-1</sup>. *Anal*. Found: C, 61.73; H, 3.92; N, 1.43. Calc. for C<sub>50</sub>H<sub>37</sub>As-Co<sub>2</sub>NO<sub>6</sub>P: C, 61.81; H, 3.84; N, 1.44%.

## 2.2. Crystal structure determinations of 2, 6, and 7

Crystals of **2** were grown by slow evaporation of a mixture solution of **2** in  $C_6H_{14}$  and  $CH_2Cl_2$ , crystals of **6** by slow diffusion of  $C_5H_{12}$  to a  $CH_2Cl_2$  solution of **6**,

and crystals of 7 by slow evaporation of 7 in  $C_6H_{14}$ , respectively. Single-crystal X-ray diffraction experiments were performed on an Enraf–Nonius CAD4 for 2 and 6 and an Enraf–Nonius CCD diffractometer for 7. Unit cells were determined by centering 25 reflections in the appropriate  $2\theta$  range. Other relevant experimental details are listed in Table 3. Structures were solved by direct methods using SHELXS-86 and refined by fullmatrix least-squares with SHELXL-93. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically using the riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached.

# 2.3. Hyperpolarizability measurement

The experiments were performed at a wavelength of 1064 nm with a mode-locked Q-switched Nd:YAG laser (Spectron SL803G). Solutions of *p*-nitroaniline in MeCN were used as internal reference ( $\beta$  (CH<sub>3</sub>CN) = 29.2 × 10<sup>-30</sup> esu) [7]. The general experimental setup is described in Ref. [2c].

# 2.4. Calculation of hyperpolarizability

The computational study of the quadratic hyperpolarizability of compounds 2-8 has been carried out with the ab initio method. The starting geometries are chosen from the experimentally determined X-ray structures 2 and 6 without further optimizations. For 7 and 8, the geometry is first optimized in the Hartree–Fock (HF) level from the starting structures based on the X-ray structures of the related structure of the series. Geometry optimization and energy calculation were carried out by the density functional (B3-LYP) method using the 3-21G\* basis set. The dipole moment and hyperpolarizability were calculated by the five-point finite difference method [7,8], which employs the results from 13 SCF calculations with the STO3G basis set on the optimized structure. Numerical calculations have been performed with the program JAGUAR 4.0 [8].

## 3. Results and discussion

## 3.1. Synthesis

Enyne dicobalt carbonyl complexes **2** and **3**, in which electron-rich (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> fragment is conjugated with an electron withdrawing organic part, have been prepared by applying the Wittig reaction to an aldehyde complex **1**, (HC=C-CHO)Co<sub>2</sub>(CO)<sub>6</sub>, using an appropriate ylide. Compound **1** has been prepared by a published procedure [6]. Treatment of **1** with ylides p-X-C<sub>6</sub>H<sub>4</sub>CH=PPh<sub>3</sub> (X = Br, NO<sub>2</sub>), generated in situ by the reaction of the corresponding phosphonium bro-



Scheme 1.

mide and KtOBu in THF, afforded (HC=C-CH=CH-C<sub>6</sub>H<sub>4</sub>-X-p)Co<sub>2</sub>(CO)<sub>6</sub> (**2**, X = Br; **3**, X = NO<sub>2</sub>) as a mixture of *E* and *Z* isomers in the ratio 1:1 (Eq. (1)).

In general, an asymmetric electron distribution, which is closely related to quadratic hyperpolarizability, is improved by increasing the strength of the electron



Chromatography of the mixture on a silica gel led to isolation of **2** and **3** with an *E* configuration in 34 and 37% yield, respectively. We expected that these compounds would fulfil the basic requirements for NLO chromophores: they contain (alkyne)Co<sub>2</sub>(CO)<sub>6</sub> as an electron donor group and nitro- or bromobenzene as an electron acceptor group, and a conjugated bridge linking the two fragments.

donor or acceptor [9]. To increase the electron donor ability of alkyne dicobalt carbonyl fragment, the  $\pi$ accepting CO ligand of **1** was replaced by a  $\sigma$ -donating phosphine ligand. Refluxing **1** with an equivalent of PPh<sub>3</sub> gave (HC=C-CHO)Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>) (**4**), as a major product. Treatment of **1** with excess PPh<sub>3</sub> afforded the doubly substituted **5** (HC=C-CHO)Co<sub>2</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> in 85% yield (Eq. (2)).

(2)



Table 1 Measured quadratic hyperpolarizabilities <sup>a</sup>

	2	3	6	7	8
$\lambda_{\max}$ (nm)	328	352	372	394	395
$\beta$ (10 <sup>-30</sup> esu)	52	84	144	227	244

<sup>a</sup> All the measurements were carried out in chloroform.

Treatment of **4** with p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH=PPh<sub>3</sub> yielded [(*E*)-(HC=C-CH=CH-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>-p)Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>) (**6**) in 76% yield as a sole product. Formation of a *Z*-isomer was not observed. When **5** was treated with p-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH=PPh<sub>3</sub>, no reaction occurred presumably due to the increased electron density on the metal.

To increase the electron density on the metal center, a carbonyl ligand in **6** was replaced by phosphine or arsine. Refluxing **6** with PPh<sub>3</sub> gave  $[(E)-(HC\equiv C-CH=CH-C_6H_4-NO_2-p)Co_2(CO)_4(PPh_3)_2]$  (7) in 91% yield and treatment of **6** with AsPh<sub>3</sub> gave  $[(E)-(HC\equiv C-CH=CH-C_6H_4-NO_2-p)Co_2(CO)_4(PPh_3)(AsPh_3)]$  (**8**) in 45% yield (Eq. (3)).

wavelength using *p*-nitroaniline in chloroform as an external standard (Table 1) [7]. The hyperpolarizability values increase in the order 2 < 3 < 6 < 7 < 8. Since all studied compounds have absorption around 532 nm, the contribution of resonance enhancement to  $\beta$  should be considered. To estimate the dispersion-corrected  $\beta$ (static hyperpolarizability,  $\beta_0$ ), the two-state model has been used [10]. The order of the static hyperpolarizability  $\beta_0$  is the same as that of  $\beta$ . Hyperpolarizability calculation has been carried out with the ab initio method. The results of the theoretical calculations are summarized in Table 2. The order of hyperpolarizability values (2 < 3 < 6 < 7 < 8) is correctly reproduced in the theoretical predictions. Considering the limitations of theoretical calculations and the uncertainties in the estimation of  $\beta_0$  from the experimental results, quantitative comparisons between them are somewhat difficult.

Molecular hyperpolarizabilities increase in the order 2 < 3, reflecting the high electron acceptability of the nitro group. This observation implies that (alky-



#### 3.2. Hyperpolarizability measurement

Chart 1 shows compounds for which hyperpolarizability measurements were made, and Table 1 shows the results. The hyperpolarizability values of all complexes were determined in chloroform at 1064 nm fundamental

ne) $Co_2(CO)_6$  fragment serves as an electron-donating group. It is not unusual for metal carbonyls to act as an electron-donating group in the second order NLO push-pull system [2].

Substitution of carbonyl ligand by weaker  $\pi$ -accepting and better  $\sigma$ -donating ligands such as PPh<sub>3</sub> and AsPh<sub>3</sub>

Table 2	
Hyperpolarizabilities for a series of compounds given in Chart 1	

	2	3	6	7	8	
$\Delta E^{a}$ (au)	0.12648	0.12628	0.11458	0.10203	0.00664	
$\mu^{\rm b}$ (au)	1.92	3.24	3.29	2.36	1.57	
$\beta_0^{\rm c} (10^{-30} {\rm esu})$	5.81	20.2	30.4	64.7	87.7	

<sup>a</sup>  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

<sup>b</sup>  $\mu$ , the dipole moment.

<sup>c</sup>  $\beta_0$ , the static obtained from the ab initio calculations.



Fig. 1. Molecular structure of 2, with the atom-labelling scheme.

leads to more electron-rich metal fragments. The order of hyperpolarizabilities of 3 < 6 < 7 < 8 is exactly coincident with that of the electron richness of metal fragment. The increased electron density of the metal center should rise with the increase of the electrondonating ability of the metal fragment and thereby enhance the molecular non-linearity. Especially, the hyperpolarizabilities of 7 and 8, in which two carbonyl ligands are substituted, are about three times larger than that of 3. Thus, the ligand substitution can be used to optimize non-linear properties.

#### 3.3. X-ray crystal structures of 2, 6, and 7

The thermal ellipsoid plots shown in Figs. 1-3 depict the structures determined in this work. Crystal data and structure refinements for **2**, **6**, and **7** are given in Table 3 and selected bond lengths and angles in Table 4. The perpendicular geometry between the C–C triple bond and the Co–Co bond is consistent with the alkynedicobalt geometry described in previous literature [11].

Single crystals of **2** were grown in a mixture solvent of hexane and dichloromethane. The coordination geometry of the metal center does not exhibit any noticeable deviation from that of regular alkyne dicobalt complexes [12]. The Co–Co bond length (2.468(2) Å) is shorter than the Co–Co bond length of 2.52 Å in  $[Co_2(CO)_8]$  [13], but is similar to Co–Co lengths found in related  $\mu$ -alkyne complexes [14]. The bond length between C1 and C2 is 1.301 Å and the dihedral angle

between C1–C2–C3 is 142.15°. The fragment –CH= CH–C<sub>6</sub>H<sub>4</sub>– of a conjugated pathway between the electron donor and acceptor is almost planar with a dihedral angle of 9.18°. The centrosymmetric nature of crystal structure of **2** (space group,  $P\bar{1}$ ) suggests that there may be no NLO behavior in the bulk phase.

Single crystals of **6** were obtained by slow diffusion of pentane to a dichloromethane solution. The bond length (2.4737(8) Å) between Co1 and Co2 is similar to that of **2**. The bond length between C1 and C2 is 1.340(5) Å, which is about 0.03 Å greater than that of **2**. The greater C1–C2 bond length of **6** may reflect the increased electron density on the metal center and suggests a larger molecular hyperpolarizability. The conjugated electron pathway  $-CH=CH-C_6H_4-$  is roughly planar with a dihedral angle of  $13.11^\circ$ . In the unit cell two enantiomers of **6** are located with an inverse relation (space group,  $P\bar{1}$ ).

Single crystals of 7 were obtained by slow evaporation of a hexane solution of 7. The bond length between Co(1) and Co(2) is lengthened to 2.4986(7) Å presumably due to the steric effects of two phosphine ligands. The presence of two *trans* phosphine ligands pushes C(1) and C(2) close to each other and the resulting bond length between C1 and C2 is 1.314(5) Å, which is about 0.02 Å shorter than that of **6**. The conjugated electron pathway  $-CH=CH-C_6H_4-$  is quite twisted with a dihedral angle of 21.04° presumably due to the ancillary ligand. It has been well known that steric interactions with the ancillary ligands bound to cobalt play a major



Fig. 2. Molecular structure of 6, with the atom-labelling scheme.

role in determining the confirmation of  $\mu$ -alkyne ligand coordinated to dicobalt [15].

The centrosymmetric nature of crystal structures of 2, 6, and 7 (space group,  $P\overline{1}$ ) suggests that there may be no NLO behavior in the bulk phase.

# 3.4. Synthesis of optically pure 6\*

As mentioned in the previous sections, compounds 2-8 exhibit a molecular response. However, due to their centrosymmetric nature in the crystal structures they do





Fig. 3. Molecular structure of 7, with the atom-labelling scheme.

not show NLO behavior in the bulk phase. Non-zero bulk NLO activity requires non-centrosymmetric crystal packing. One way to ensure non-centrosymmetric crystal packing is to introduce chiral element(s) into the molecule. Thus, we synthesized optically pure  $6^*$ .

Diastereomer **9**\* of [(-)-mentyl-propargyl ether]Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>) was prepared and separated according to a published procedure [16]. The molecular crystal structure of **9**\* was determined by X-ray diffraction study. Nicholas reaction [17] of **9**\* followed by Swern oxidation gave an enantiomerically pure [(HC=C-CHO)Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>)] (**4**\*), in 28% yield. Wittig reaction of **4**\* with *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C=PPh<sub>3</sub> gave an optically pure [((*E*)-HC=C-CH=CH-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>-*p*)Co<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>)] (**6**\*), in 82% yield (Eq. (4)).

The optical purity of  $6^*$  could be confirmed by chiral HPLC. Unfortunately,  $6^*$  is an oily compound. Thus, we could not measure the SHG of  $6^*$ . It was slowly racemized at room temperature to give a solid compound.

#### 4. Conclusion

In this paper we have synthesized a series of new donor-acceptor compounds of the form  $[(HC=C-CH=CH-C_6H_4-X-p)Co_2(CO)_4(L^1)(L^2)]$  (2, X = Br,  $L^1 = L^2 = CO$ ; 3,  $X = NO_2$ ,  $L^1 = L^2 = CO$ ; 6,  $X = NO_2$ ,  $L^1 = CO$ ,  $L^2 = PPh_3$ ; 7,  $X = NO_2$ ,  $L^1 = L^2 = PPh_3$ ; 8,  $X = NO_2$ ,  $L^1 = AsPh_3$ ,  $L^2 = PPh_3$ ). The concept of using the (alkyne)Co<sub>2</sub>(CO)<sub>4</sub>(L<sup>1</sup>)(L<sup>2</sup>) moiety as an electron donor was rewarded by high  $\beta$  values of complexes with good  $\sigma$ -donor and poor  $\pi$ -acceptor ligands  $L^1$  and  $L^2$ . Transformation of 2 into 8 led to five times increase of  $\beta$  values. An optically pure 6\* has been synthesized but racemized slowly at room temperature.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 3 Crystal data and refinement for **2**, **6** and **7** 

	2	6	7
Empirical for- mula	C <sub>16</sub> H <sub>7</sub> BrCo <sub>2</sub> O <sub>6</sub>	C <sub>33</sub> H <sub>22</sub> Co <sub>2</sub> NO <sub>7</sub> P	C <sub>50</sub> H <sub>37</sub> Co <sub>2</sub> NO <sub>6</sub> P <sub>2</sub>
Formula weight	492.99	693.35	927.61
Crystal system	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ
a (Å)	6.8109(10)	9.6315(12)	9.9966(5)
b (Å)	7.7813(10)	10.026(2)	12.8973(6)
c (Å)	17.6658(10)	18.899(5)	18.3542(8)
α (°)	80.051(10)	97.92(2)	79.433(3)
β(°)	86.534(10)	96.59(2)	89.428(3)
γ (°)	76.257(10)	118.059(13)	69.590(2)
V (Å <sup>3</sup> )	895.6(2)	1561.0(6)	2176.47(18)
Ζ	2	2	2
$D_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.828	1.475	1.415
$2\theta$ Range (°)	2.34-24.97	2.22-24.97	5.06-27.48
No. total col- lection	3154	5828	14013
No. unique data	2867	5464	9366
No. parameter refined	237	401	554
$R_1$	0.0729	0.0535	0.0579
$wR_2$	0.1869	0.1512	0.1105
Goodness-of- fit	1.072	0.135	1.072

Data Centre, CCDC Nos. 167569(7), 167570(2), and 167571(6) for compounds **2**, **6**, and **7**, respectively (tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and observed and calculated structure factors). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK

Table 4 Selected bond distances (Å) and angles (°) for  $\mathbf{2}, \mathbf{6}$  and  $\mathbf{7}$ 

(fax: +44-1223-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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2		6		7	
Bond distances					
Co(1) - C(1)	1.931(12)	Co(1) - C(1)	1.937(4)	Co(1) - C(1)	1.951(4)
Co(1)-Co(2)	2.468(2)	Co(1)-Co(2)	2.4737(8)	Co(1)-Co(2)	2.4986(7)
Br-C(8)	1.88(10)	Co(1)-C(01)	1.783(4)	Co(2) - P(2)	2.2252(11)
Co(1) - C(2)	1.980(9)	Co(1) - C(2)	1.956(4)	N(1) - C(8)	1.469(5)
Co(2) - C(1)	1.938(10)	Co(2) - C(1)	1.976(4)	Co(1) - C(2)	1.977(4)
Co(1)-C(05)	1.780(10)	C(1) - C(2)	1.336(5)	Co(2) - C(1)	1.945(4)
C(1) - C(2)	1.313(14)	Co(1)-P(2)	2.2055(11)	Co(1) - C(11)	1.776(4)
Co(2) - C(2)	1.985(8)	Co(2) - C(2)	1.978(4)	N(1)-O(5)	1.205(5)
		C(8) - N(1)	1.459(6)	Co(1) - P(1)	2.2254(10)
				Co(2) - C(2)	1.982(3)
				C(1) - C(2)	1.314(5)
Bond angles					
C(1) - C(2) - C(3)	139.5(12)	Co(1) - C(2) - Co(2)	77.93(13)	C(1)-C(2)-C(3)	147.8(4)
Co(2) - C(1) - Co(1)	79.34(4)	C(1)-C(2)-C(3)	142.3(4)	Co(2)-C(1)-Co(1)	79.78(14)
Co(1) - C(2) - Co(2)	77.6(3)	Co(1) - C(1) - Co(2)	78.44(14)	Co(1) - C(2) - Co(2)	78.26(12)

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