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A new route to seleno and telluro esters by $Co_2(CO)_8$-mediated and -catalyzed carbonylation of diaryl diselenides and ditellurides with carbon monoxide

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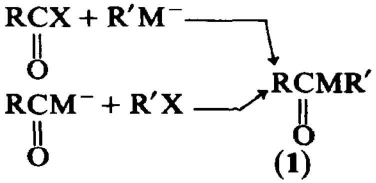
Abstract

Diaryl diselenides react with CO (5–100 atm) at 100–200 °C during 1–4 h in the presence of $Co_2(CO)_8$ to give the corresponding aryl selenocarboxylic acid esters in 21–96% yields. Similar treatment of diphenyl ditelluride gives the telluro analogues in lower yields. Didodecyl diselenide also gives the corresponding seleno ester, while esters were not produced from dibenzyl diselenide and didodecyl ditelluride. Under milder conditions (10 atm CO/125 °C/1 h) the reactivity of $(PhM)_2$ (M = S, Se, Te) for the corresponding esters was found to be in the order Te > Se > S. The carbonylation of diaryl diselenides proceeds catalytically in $Co_2(CO)_8$ in the presence of triphenylphosphine. It was shown unambiguously that benzoylcobalt tetracarbonyl, which is one of the possible intermediates when aryl is phenyl, reacts smoothly with diphenyl diselenide or ditelluride to give the corresponding ester, phenyl selenobenzoate or tellurobenzoate, respectively, in a good yield.

Introduction

Seleno- and telluro-carboxylic acid esters (1) [1] (abbreviated as seleno and telluro esters) are attractive compounds because of their liquid-crystal properties [2] and are known to block a number of different nerve impulses [3]. The radical-induced degradation of seleno esters derived from carboxylic acids to nor-alkanes has also found use in an efficient synthesis of some steroids [4]. Several procedures to make these esters have been developed, but they usually require the use of compounds bearing carbonyl groups such as RCOX (X = halogen) or $RCOM^-$ (M = Se, Te) as starting substrates (eq. 1). However, up to now, no methods



$$\left.\begin{array}{l} \mathrm{R\underset{\underset{O}{\|}}{C}X} + \mathrm{R'M^-} \\ \mathrm{R\underset{\underset{O}{\|}}{C}M^-} + \mathrm{R'X} \end{array}\right\} \longrightarrow \underset{(\mathbf{1})}{\mathrm{R\underset{\underset{O}{\|}}{C}MR'}} \qquad (M = Se, Te; X = halogen) \qquad (1)$$

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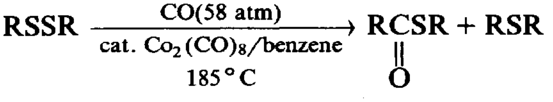
involving the use of carbon monoxide(CO) as a carbonyl source have been developed. Alper et al. recently reported that the dicobalt octacarbonyl ($Co_2(CO)_8$)-catalyzed carbonylation of diaryl or dibenzyl disulfides with pressurized CO at high temperature gives the corresponding thioesters (eq. 2) [5]. The bond energy of the S–S bond is smaller than that of the C–S bond, and in fact Alper et al. have proposed that S–S bond fission takes place in the initial stages of the reaction.



$$RSSR \xrightarrow[\text{cat. } Co_2(CO)_8/\text{benzene},\ 185\,°C]{CO(58\text{ atm})} R\underset{\underset{O}{\|}}{C}SR + RSR \qquad (2)$$

$(R = Ar, ArCH_2)$

We thought that similar carbonylations of the corresponding diselenides and ditellurides might proceed under milder conditions or even in absence of catalyst, because the Se–Se (184 kJ/mol) and Te–Te (138 kJ/mol) bonds are much weaker than the S–S (213 kJ/mol) bond [6]. As part of a series of studies on organoselenium and organotellurium chemistry [7] we describe here the results of the synthesis of seleno and telluro esters from diorganyl diselenides and ditellurides by carbonylation with CO [8].

Results and discussion

We first studied the carbonylation of diphenyl diselenide and ditelluride with 1–50 atm CO in acetonitrile or benzene at 20–150 °C for 1 h in absence of catalyst, but almost all of the starting compounds were recovered intact. We then selected various transition metal carbonyls and salts as catalysts (5–100 mol%) for the carbonylation of diphenyl diselenide (**2a**) with 100 atm CO at 200 °C in acetonitrile (eq. 3). The results listed in Table 1 indicate that $Co_2(CO)_8$ is the best catalyst for the preparation of phenyl selenobenzoate (**3a**), that $Co(OAc)_2 \cdot 4H_2O$, $Mn_2(CO)_{10}$, $Mn(CO)_5Br$, and $Pd(PPh_3)_4$ are only slightly effective, and that compounds such as $Mo(CO)_6$, $Rh_6(CO)_{16}$, $RuCl_3$, $CoCl_2 \cdot 6H_2O$, Li_2PdCl_4, and $PtCl_2 \cdot 6H_2O$ are ineffective. The yield of **3a**, which increased, with increase in the amount of $Co_2(CO)_8$ present and with shorter reaction times, was almost quantitative based on the amount of **2a** charged when the reaction was carried out for 1 h using 40 mol% of $Co_2(CO)_8$, but the reaction was only slightly catalytic. Benzene and tetrahydrofuran were good solvents, but in methanol or aqueous acetonitrile only diphenyl selenide (**4a**) was formed. Several results in Table 1 using $Co_2(CO)_8$ catalyst also show that the ester **3a** is not very stable under the reaction conditions employed, with $Co_2(CO)_8$ as catalyst, and it is necessary to stop the reaction after a while in order to obtain a high yield of **3a**. When **3a** was prepared separately and

$$RMMR + CO \xrightarrow[MeCN]{\text{catalyst}} R\underset{\underset{O}{\|}}{C}MR + RMR \qquad (3)$$

(2) (3) (4)

(**2a**, R = Ph, M = Se; **2b**, $R = 4\text{-}MeOC_6H_4$, M = Se;

2c, $R = PhCH_2$, M = Se; **2d**, $R = n\text{-}C_{12}H_{25}$, M = Se; **2e**, R = Ph, M = Te;

2f, $R = 4\text{-}MeOC_6H_4$, M = Te; **2g**, $R = n\text{-}C_{12}H_{25}$, M = Te)

Table 1

Effect of the catalyst on the formation of phenyl selenobenzoate (**3a**) [a]

Catalyst (mmol)		Reaction time (h)	Conversion of **2a** [b] (%)	Product and yield (%) [c]	
				3a	**4a**
$Co_2(CO)_8$	0.05	4	22	12(240)	3
$Co_2(CO)_8$	0.2	4	53	43(215)	3
$Co_2(CO)_8$	0.2	12	53	29(145)	6
$Co_2(CO)_8$	0.4	1	98	96(240)	2
$Co_2(CO)_8$	0.5	4	98	53(115)	4
$Co(OAc)_2 \cdot 4H_2O$	0.8	1	87	24(30)	1
$Mn_2(CO)_{10}$	0.4	1	34	9(23)	11
$Mn(CO)_5Br$	1.0	1	38	3(3)	15
$Pd(PPh_3)_4$	0.05	1	25	7(140)	4

[a] Carried out with **2a** (1 mmol) and catalyst in acetonitrile (5 ml) at 200 ° C under 100 atm CO. [b] Determined by GLC. [c] The yields are based on amount of **2a** charged (by GLC). The yields based on the catalyst are shown in parentheses.

was treated with 40 mol% $Co_2(CO)_8$ in acetonitrile under 100 atm CO at 200 ° C for 4 h, it was converted completely to a small amount of **4a** and some unidentified compounds.

In order to find out whether this $Co_2(CO)_8$-mediated carbonylation can proceed under milder conditions, the reactions of **2a** with lower pressures of CO at lower temperatures were carried out in the presence of 40 mol% of $Co_2(CO)_8$ for various reaction times. The results listed in Table 2 indicate that with 10 atm CO at 150 ° C or with 50 atm CO at 125 ° C **3a** was obtained in good yield, and even with 10 atm CO at 125 ° C **3a** was produced in 35% yield. In all cases a small amount of **4a** was found to be present amongst the products. Under much milder conditions, i.e., with 1 atm of CO in refluxing acetonitrile or with 50 atm CO at room temperature, **3a** was scarcely formed. At higher temperatures the longer reaction times resulted in a decrease in the amount of **3a** as described above, whereas at lower temperature the

Table 2

Effect of temperature, time, and CO pressure on carbonylation of **2a** [a]

Reaction temperature (° C)	CO pressure (atm)	Reaction time (h)	Conversion of **2a** [b] (%)	Product and yield (%) [c]	
				3a	**4a**
100	50	1	84	21	9
100	50	5	96	57	trace
125	10	1	93	35	9
125	50	1	93	57	trace
150	5	1	94	23	2
150	10	1	84	58	2
150	100	1	98	68	trace
200	50	1	94	85	4
200	100	1	98	96	2
200	100	4	94	82	2

[a] Carried out with **2a** (1 mmol) and $Co_2(CO)_8$ (0.4 mmol) in acetonitrile (5 ml). [b] Determined by GLC. [c] The yields are based on amount of **2a** charged (by GLC).

Table 3

Carbonylation of various diaryl and dialkyl diselenides and ditellurides [a]

2	CO (atm)	Reaction temperature (°C)	Conversion of **2** [b] (%)	Product and yield (%) [c]	
				3	**4**
2a	20	150	90	69	1
2b	20	150	71	49	3
2b	50	150	90	36	16
2b	100	175	81	41	4
2c	50	150	89	0	88 [d]
2d	100	200	89	32	51
2e	10	125	88	24	23
2e	50	125	83	34	13
2e	100	125	94	52	13
2e	100	150	99	15	33
2g	100	125	89 [d]	0	71 [e]

[a] Carried out with **2** (1 mmol) and $Co_2(CO)_8$ (0.4 mmol) in acetonitrile (5 ml) for 1 h. [b] Determined by GLC. [c] The yields are based on amount of **2** charged (by GLC). [d] Determined by ^1H NMR. [e] Isolated yield.

inverse occurred. Thus, increasing the reaction time from 1 to 5 h at 100 °C improved the yield of **3a** almost three times in spite of almost the same conversion of **2a** and this suggests that seleno-ester formation ceases at some, as yet unknown, stage of the reaction. In fact, when the reaction mixture was stirred for another hour at 200 °C after treatment of **2a** with 50 atm CO in acetonitrile at 100 °C for 1 h (**3a** 21% and **4a** 9%; see Table 2), **3a** and **4a** were produced in 63 and 10% yields, respectively.

The carbonylation of other diselenides and some ditellurides was carried out under the optimal conditions for production of **3a**, namely with 40 mol% $Co_2(CO)_8$ and 10–100 atm CO in acetonitrile at 125–200 °C for 1 h (see Tables 1 and 2), for which the results are shown in Table 3. The CO insertion did not occur with dibenzyl diselenide (**2c**), dibenzyl selenide (**4c**) being the sole product in this case. Di-n-dodecyl diselenide (**2d**) did give the selenoester **3d**, but the main product was di-n-dodecyl selenide (**4d**). In the case of diphenyl ditelluride (**2e**) the expected telluroester (**3e**) was obtained together with diphenyl telluride (**4e**), but the bis(4-methoxyphenyl) ditelluride (**2f**) scarcely gave the corresponding telluroester (**3f**) (determined by IR and NMR). The yield of the telluroester was generally lower than that of the selenoester and the former was also found to be unstable under the reaction conditions employed. No telluroester was produced from di-n-dodecyl ditelluride (**2g**) and instead the corresponding monotelluride (**4g**) was formed in a high yield.

The first step of the carbonylation is probably fission of the M–M bond in the dichalcogenides (**2**). It is expected that the reactivity of **2** increases in the order Te > Se > S if their bond energies are taken into account. Since the product esters are not stable under severe reaction conditions, we studied the behavior of the three diphenyl dichalcogenides (**2**; R = Ph) in regard to this carbonylation under relatively mild conditions (10 atm CO/125 °C/1 h) in acetonitrile and in benzene. Comparison of the total yield of each ester (**3**) and monochalcogenide (**4**) shown in Table 4 indicates that the ditelluride and diselenide are more reactive than the

Table 4

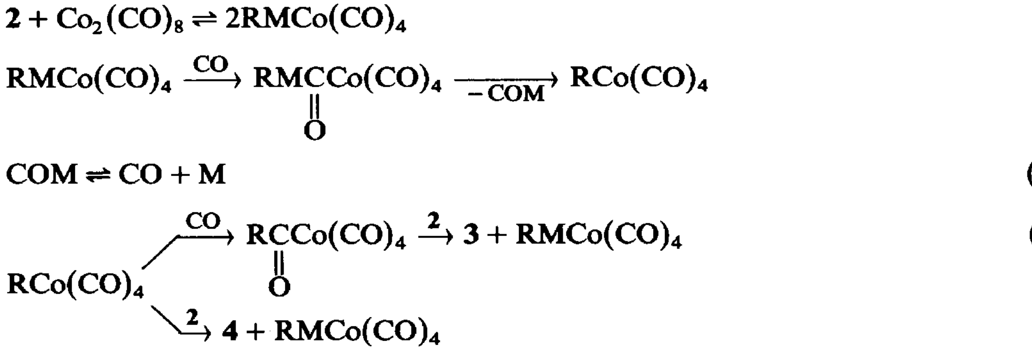
Comparison of the reactivity of 2 (R = Ph) in its reaction with CO [a]

2 (R = Ph) M	Solvent	Conversion of 2 [b] (%)	Product and yield (%) [c]	
			3 (R = Ph)	4 (R = Ph)
S	MeCN	97	trace	trace
S	C_6H_6	68	10	trace
Se [d]	MeCN	93	35	9
Se [d]	C_6H_6	88	20	11
Te [e]	MeCN	88	24	23
Te [e]	C_6H_6	88	32	25

[a] Carried out with 2 (R = Ph) (1 mmol) and $Co_2(CO)_8$ (0.4 mmol) in solvent (5 ml) at 125 °C for 1 h under 10 atm CO. [b] Determined by GLC. [c] The yields are based on amount of 2 (R = Ph) charged (by GLC). [d] Corresponds to **2a**. [e] Corresponds to **2e**.

disulfide and this is enhanced in benzene as solvent. In order to minimize the unwanted side-reactions of the products with $Co_2(CO)_8$, the reactions using 5 mol% of $Co_2(CO)_8$ were also attempted at 125 °C for 1 h, but all reactions were too slow, and gave too little product so that their reactivities could not be compared.

The carbonylation probably proceeds as depicted in Scheme 1 (steps i–v) and follows closely the scheme proposed by Alper et al. [5]. Of these steps, we confirmed here step iv for the first time. Thus, a benzoylcobalt compound, prepared in situ by a standard procedure [9], reacts with either of the three diphenyl



$$2 + Co_2(CO)_8 \rightleftharpoons 2RMCo(CO)_4 \qquad (i)$$

$$RMCo(CO)_4 \xrightarrow{CO} RM\underset{\overset{\|}{O}}{C}Co(CO)_4 \xrightarrow[-COM]{} RCo(CO)_4 \qquad (ii)$$

$$COM \rightleftharpoons CO + M \qquad (iii)$$

$$RCo(CO)_4 \xrightarrow{CO} R\underset{\overset{\|}{O}}{C}Co(CO)_4 \xrightarrow{2} 3 + RMCo(CO)_4 \qquad (iv)$$

$$RCo(CO)_4 \xrightarrow{2} 4 + RMCo(CO)_4 \qquad (v)$$

Scheme 1

dichalcogenides 2 (R = Ph; M = S, Se, Te) under atmospheric CO to produce the relevant ester 3 (R = Ph) in good yields (Table 5) (eq. 4).

$$Co_2(CO)_8 + NaH \rightarrow [NaCo(CO)_4] \xrightarrow[\text{THF, CO}]{\text{PhCOCl}} [PhCOCo(CO)_4] \xrightarrow[\text{THF, CO}]{2\ (R = Ph)}$$

$$\underset{(3:\ R = Ph)}{PhCOMPh} + \underset{(4:\ R = Ph)}{PhMPh} \qquad (4)$$

In the cases of disulfides the reaction of the disulfides proceeds catalytically in $Co_2(CO)_8$ [5], whereas catalysis by cobalt compound in the carbonylation of the diselenides and the ditellurides was poor. One reason might be that the $Co_2(CO)_8$ is poisoned by the selenium or tellurium which may be liberated by steps ii and iii of Scheme 1. In fact, after the carbonylation a black solid was always formed and an analysis of the solid obtained from the reaction of **2a** or **2e** revealed that it was

Table 5

Reactions of $PhCOCo(CO)_4$ with **2** (R = Ph) [a]

2 (R = Ph) M	Reaction time (h)	Product and yield (%) [b]	
		3 (R = Ph)	**4** (R = Ph)
S	20	48(60)	trace
Se	1	21(26)	trace
Se	20	45(56)	4
Se	96	47(59)	6
Te	1	trace	7
Te	20	32(40)	15
Te	96	67(84)	18

[a] Carried out with **2** (R = Ph) (1 mmol) and $PhCOCo(CO)_4$ (0.8 mmol) in THF (10 ml) at 0 °C under 1 atm CO. [b] The yields (by GLC) are based on amount of **2** (R = Ph) charged; the yields based on amount of $PhCOCo(CO)_4$ charged are shown in parentheses.

mainly elemental selenium and cobalt or elemental tellurium and cobalt, respectively (see Experimental). In order to find out whether the catalyst was being poisoned, the carbonylations were carried out in the presence of commercial selenium or tellurium powder. Under the reaction conditions which usually give yields of **3a** of 96% from **2a** (see Table 1), the addition of 1/2 and 1 equivalent of selenium powder to **2a** resulted in a decrease in the yield of **3a** to 70 and 58%, respectively. Similarly, when 1 equivalent of tellurium powder was added to **2e** under the conditions which usually give yields of **3e** of 49% (see Table 3), the carbonylation of **2e** yielded no **3e** and, **4e** was formed in 15% yield. These results support the above speculation that the elemental selenium or tellurium, that is liberated during the reaction, deactivates the cobalt catalyst. Thus, if these elements could be trapped in some way, the carbonylation would be more effective. It is known that triphenylphosphine reacts with selenium [10], but not with tellurium [11], to form triphenylphosphine selenide (eq. 5), whereas tellurium interacts with a stronger donor such as tri-n-butylphosphine [11] or hexamethyl phosphorous triamide [12] to give the corresponding phosphine telluride (eq. 6). Hoping that the effects of $Co_2(CO)_8$ become catalytic, we carried out the carbonylations of the diselenides and ditellurides in the presence of triphenylphosphine, or other donor

$$PPh_3 + Se \xrightarrow{\Delta} Ph_3P{=}Se \tag{5}$$

$$P(n\text{-}Bu)_3 \text{ or } P(NMe_2)_3 + Te \xrightarrow{\Delta} (n\text{-}Bu)_3P{=}Te \text{ or } (Me_2N)_3P{=}Te \tag{6}$$

compound, for which typical results are shown in Table 6. The data show that triphenylphosphine, when added to the reaction mixture makes the carbonylation of diselenides catalytic in $Co_2(CO)_8$, and increases the yield of the selenoester as the amount of phosphine added is increased. It is possible that triphenylphosphine reacts with $Co_2(CO)_8$ to give hexacarbonylbis(triphenylphosphine)dicobalt, $[Co(CO)_3(PPh_3)]_2$, which could be the more active catalyst in this reaction. However, when commercially available $[Co(CO)_3(PPh_3)]_2$ was used, little carbonylation of **2a** at 150 °C under 5 atm CO was observed, and the addition of triphenylphosphine to this carbonylation system resulted in a greatly improved yield of **3a** (see Table 6). These results show that although $Co_2(CO)_8$ may be present as some

Table 6

Effects of additives for $Co_2(CO)_8$-catalyzed carbonylation of **2a**, **2b**, and **2a** [a]

2 (1 mmol)	CO (atm)	Reaction temperature (°C)	Co Catalyst [b] (mmol)	Additive (mmol)	Conversion of **2** [c] (%)	Product and yield (%) [d]	
						3	**4**
2a	10	150	0.1	–	21	6(60)	1
2a	10	150	0.1	PPh_3 0.5	49	48(480)	trace
2a	10	150	0.1	$AsPh_3$ 0.5	20	6(60)	trace
2a	10	150	0.1	$BiPh_3$ 0.5	36	25(250)	7
2a	10	150	0.1	$P(OPh)_3$ 0.5	28	19(190)	1
2a	10	150	0.1	$P(n\text{-}Bu)_3$ 0.5	38	22(220)	trace
2a	5	150	0.1	PPh_3 0.5	47	40(400)	1
2a	10	150	0.1 [e]	–	33	20(200)	trace
2a	10	150	0.1 [e]	PPh_3 0.3	55	48(480)	1
2a	5	150	0.05 [e]	–	10	3(60)	1
2a	100	200	0.05	–	16	7(140)	6
2a	100	200	0.05	PPh_3 0.2	35	28(560)	trace
2a	100	200	0.05	PPh_3 0.5	60	54(1080)	trace
2a	100	200	0.05	PPh_3 1.0	60	46(920)	trace
2a	100	200	0.01	PPh_3 0.5	20	20(200)	0
2b	20	150	0.1	PPh_3 1.0	36	29(290)	2
2e	100	125	0.1	–	88	24(240)	23
2e	100	125	0.1	PPh_3 0.5	15	0	15
2e	100	125	0.1	$P(n\text{-}Bu)_3$ 1.0	25	0	21
2e	100	125	0.1	$P(NMe_2)_3$ 1.0	23	0	22

[a] Carried out in acetonitrile (5 ml) for 1 h. [b] $Co_2(CO)_8$ unless otherwise stated. [c] Determined by GLC. [d] The yields are based on amount of **2** charged (by GLC). The yields are based on amount of cobalt catalyst charged are shown in parentheses. [e] $[Co(CO)_3(PPh_3)]_2$ was used as the Co catalyst.

phosphine complex, its reactivity is similar to $Co_2(CO)_8$ and that most important role played by the triphenylphosphine is to trap elemental selenium liberated. In the case of **2e**, on the other hand, the addition of any phosphine completely stopped the formation of the telluroester and almost all of compound **2e** was converted to the monotelluride (**4e**). Attempts to carry out the carbonylation of the ditellurides catalytically in $Co_2(CO)_8$ failed.

Experimental

^1H NMR spectra were recorded on a Hitachi/Perkin–Elmer R-600 (60 MHz), JEOL JNM FX-100(100 MHz), and Varian VXR 200(200 MHz) spectrometers as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. The coupling constants (J) are in hertz (Hz). IR spectra were recorded on Perkin–Elmer 521 and JASCO IR-810 infrared spectrophotometers as KBr pellets (for solids) or thin films (for liquids). Mass spectra were measured on a JEOL JMS-DX mass spectrometer. Inductively coupled plasma emission spectroscopy (ICPES) for determination of metal concentration was carried out on Nippon Jarrell-Ash ICPES, Model ICAP-500. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses (1 m × 0.5 cm columns packed with 5% Silicone DC QF-1 and 5% EGSS-X on Chromosorb-W 60–80 mesh) were carried out on a Yanaco G 2800 instrument with flame-ionization detectors and N_2 as carrier gas. *trans,trans*-1,4-Diphenyl-1,3-butadiene was used as the internal standard for the determination of sulfur and selenium compounds, while benzyl phenyl ketone was used for the tellurium compounds. All column chromatography was carried out using Wakogel C-200 (100–200 mesh). For preparative chromatography plates precoated with Merck silica gel 60 F_{254} of 2-mm thickness were used.

Materials

Solvents were freshly distilled before use: methanol was distilled from magnesium methoxide prepared in situ from Mg, iodine, and methanol; acetonitrile and benzene were distilled from CaH_2; tetrahydrofuran was distilled from sodium benzophenone ketyl under N_2. Inorganic metal salts as well as the organometallic compounds such as $Co_2(CO)_8$, $[Co(CO)_3(PPh_3)]_2$, $Mn_2(CO)_{10}$, $Mn(CO)_5Br$, $Mo(CO)_6$, $Rh_6(CO)_{16}$, and $Pd(PPh_3)_4$ were all commercial products and were used without prior purification. Diphenyl sulfide, diphenyl selenide (**4a**), diphenyl telluride (**4e**), diphenyl disulfide, and diphenyl diselenide (**2a**) were commercial products. The compounds to be studied were prepared by published procedures: dibenzyl diselenide (**2c**) [13], di-n-dodecyl diselenide (**2d**) [14], diphenyl ditelluride (**2e**) [15], bis(4-methoxyphenyl) ditelluride (**2f**) [16], benzoyl phenyl selenide (**3a**) [17], benzoyl phenyl telluride (**3e**) [18], bis(4-methoxyphenyl) selenide (**4b**) [19], dibenzyl selenide (**4c**) [20], di-n-dodecyl selenide (**4d**) [21], and di-n-dodecyl telluride (**4g**) [22].

Bis(4-methoxyphenyl) diselenide (**2b**) was prepared by a published method [23] from Mg (0.486 g, 20 mmol), 4-MeOC_6H_4I (4.68 g, 20 mmol), and Se (1.58 g, 20 mmol), but **2b** was obtained as a mixture with a minor amount of bis(4-methoxyphenyl) selenide (**4b**) (3/1 by GLC, ca. 4 g). Each diselenide and the monoselenide was isolated pure by use of the procedure as follows. The mixture was stirred with rongalite (1.54 g, 10 mmol) and NaOH (1.2 g, 20 mmol) in distilled water (50 ml) under N_2 at room temperature. After 24 h the monoselenide in the solution was extracted under N_2 with diethyl ether (7 × 30 ml) by syringe. The extract was washed with brine and dried over $MgSO_4$. Evaporation left the yellow solid of pure **4b** (0.80 g, 27% yield), m.p. 48–51°C; ^1H NMR; $\delta(H)$ (60 MHz) 3.76(6H, s), 6.80(4H, d, J 9.0 Hz), 7.40(4H, d, J 9.0 Hz). Anal. Found: C, 57.29; H, 4.84. $C_{14}H_{14}O_2Se$ calcd.: C, 57.35; H, 4.81%. The red homogeneous aqueous layer was poured into distilled water (100 ml) and the mixture was acidified with conc. HCl and extracted with diethyl ether (3 × 100 ml). The extract was washed with brine and then dried over $MgSO_4$. Evaporation of the solvent left the red oil of pure **2b** (1.41 g, 38% yield); ^1H NMR; $\delta(H)$ (60 MHz) 3.75(6H, s), 6.76(4H, d, J 9.0 Hz), 7.50(4H, d, J 9.0 Hz). Anal. Found: C, 44.79; H, 3.70. $C_{14}H_{14}O_2Se_2$ calcd.: C, 45.18; H, 3.79%.

Di-n-dodecyl ditelluride (**2g**) was prepared by the reaction of n-dodecyl bromide (1.25 g, 5 mmol) in ethanol (10 ml) with Na_2Te_2 in water at reflux for 30 min. (The Na_2Te_2 had been prepared in situ from Te powder (1.27 g, 10 mmol), rongalite (0.77 g, 5 mmol), and NaOH (0.4 g, 10 mmol) in degassed water (10 ml) at reflux for 1 h under N_2 [24*]. After normal work-up, evaporation of the ether extract and

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* Reference number with asterisk indicates a note in the list of references.

washing with cold acetone a red solid of pure **2g** remained (0.79 g, 1.33 mmol, 53% yield); m.p. 35–37 °C, ^{1}H NMR; δ(H) (200 MHz) 0.88(6H, t, *J* 6.2 Hz), 1.2–1.35(36H, m), 1.65–1.8(4H, m), 3.10(4H, t, *J* 6.2 Hz). Anal. Found: C, 48.28; H, 8.57. $C_{24}H_{50}Te_2$ calcd.: C, 48.54; H, 8.49%.

General procedure for the carbonylation of diorganyl diselenides or ditellurides with pressurized carbon monoxide

In a stainless steel autoclave equipped with an internal teflon vessel were placed diorganyl diselenide or ditelluride (1 mmol), $Co_2(CO)_8$ (0.01–0.5 mmol), triphenylphosphine (0–1 mmol), and solvent (5 ml). The system was then flushed and filled with CO (5–100 atm) and the mixture was stirred at a known temperature for an appropriate length of time. Cooling the solution to room temperature gave a black precipitate, which was filtered off. The products in the filtrate were determined directly by GLC using a Silicone DC QF-1 5% (1 m) column with an internal standard. To isolate the product ester, the filtrate was stripped of the solvent and the oily residue was subjected to column chromatography on SiO_2 or to preparative TLC.

The black solid obtained from the carbonylation of **2a** (0.312 g, 1 mmol) with CO (100 atm) in the presence of $Co_2(CO)_8$ (0.138 g, 1.4 mmol) at 200 °C for 1 h was washed with diethyl ether and dried in vacuo (0.086 g). This was IR inactive and contained very little C, H, and N (by combustion analysis). ICPES of the solid revealed the presence of selenium (64.2%) at 196.026 nm and cobalt (28.8%) at 238.892 nm. Almost the same result was obtained in the case of **2e**; tellurium was determined at 238.578 nm.

Benzoyl phenyl selenide (3a). 313 mg (1.2 mmol, 60% yield) of **3a** was isolated by column chromatography (hexane as eluent) by the reaction of **2a** (2 mmol) with CO (100 atm) in acetonitrile (10 ml) in the presence of $Co_2(CO)_8$ (0.8 mmol) at 200 °C for 1 h. Yellow solid, m.p. < 30 °C; ^{1}H NMR; δ(H) (200 MHz) 7.4–7.6 (6H, m), 7.91 (2H, d, *J* 1.4 Hz), 7.95 (2H, d, *J* 1.4 Hz); high-resolution mass spectrum, M^+ calcd. for $C_{13}H_{10}OSe$ 261.9896 and 259.9905, found 261.9911 and 259.9943.

4-Methoxybenzoyl 4-methoxyphenyl selenide (3b). **3b** with hexane/ethyl acetate (5/1) as eluent, was isolated as a yellow solid, m.p. 111–113 °C, ^{1}H NMR; δ(H) (60 MHz) 3.80(3H, s), 3.84(3H, s), 6.94(4H, d, *J* 9 Hz), 7.50(2H, d, *J* 9 Hz), 7.92(2H, d, *J* 9 Hz): IR(KBr) 2960, 2930, 2840, 1680(s), 1660(s), 1590(s), 1490(s), 1450, 1310, 1290, 1270(s), 1250(s), 1210(s), 1180(s), 1020(s), 880(s), 830(s), 820, 810, 780, 610 cm^{-1}. Found: C, 55.92; H, 4.41. $C_{15}H_{14}O_3Se$ calcd.: C, 56.08; H, 4.39%.

n-Dodecyl-n-tridecanoyl selenide (3d). **3d** with hexane as eluent, was isolated as white crystals, m.p. < 30 °C, ^{1}H NMR; δ(H) (200 MHz) 0.87(6H, t, *J* 6.8 Hz), 1.2–1.7(40H, m), 2.60(2H, t, *J* 7.5 Hz), 2.88(2H, t, *J* 7.3 Hz); IR(KBr) 2950, 2920(s), 2850(s), 1710(s), 1460, 720 cm^{-1}. Anal. Found: C, 67.00; H, 11.22. $C_{25}H_{50}OSe$ calcd.: C, 67.38; H, 11.31%.

Carbonylation with an atmospheric pressure of carbon monoxide

In a two-necked 50-ml round-bottom flask, equipped with a septum inlet, a three-way stopcock, and a reflux condenser, were placed diphenyl diselenide or ditelluride (1 mmol) and $Co_2(CO)_8$ (0.05–0.4 mmol). The system was flushed with CO from a CO-filled balloon connected to the flask at 25 °C, and dry acetonitrile (5 ml) was added by syringe. After the mixture had been stirred for 1–20 h at room or reflux temperature, a small amount of a black precipitate was filtered off and the products in the filtrate were analyzed by GLC.

*Reactions of benzoylcobalt tetracarbonyl [$PhCOCo(CO)_4$] with diphenyl disulfide, **2a**, and **2e** (Table 5).*

In a two-necked 50-ml round-bottom flask, equipped with a septum inlet and a three-way stopcock, was placed diphenyl dichalcogenide (1 mmol). The system was then flushed with CO from a CO-filled balloon connected to the flask at 25 ° C, and a THF (10 ml) solution of benzoylcobalt tetracarbonyl (0.8 mmol), prepared separately by a standard method [9] from benzoyl chloride, $Co_2(CO)_8$, and NaH under N_2, was added by syringe. After the mixture had been stirred for an appropriate length of time at room temperature, a precipitate was filtered off and the products in the filtrate were determined directly by GLC.

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References

1 S. Kato, T. Murai and M. Ishida, Org. Prep.&Pro. Int., 18 (1986) 369.
2 G. Heppke, J. Martens, K. Praefcke and H. Simon, Angew. Chem. Int. Ed. Engl., 16 (1977) 318.
3 S.-H. Chu and H.G. Mautner, J. Med. Chem., 11 (1968) 446.
4 J. Pfenninger and W. Graf, Helv. Chim. Acta, 63 (1980) 1562; J. Pfenninger, C. Heuberger and E. Graf, ibid., 63 (1980) 2328.
5 S. Antebi and H. Alper, Tetrahedron Lett., 26 (1985) 2609.
6 L. Pauling, The Nature of the Chemical Bond, 3rd edit., Cornell Univ. Press, 1960, p. 85.
7 For example: K. Ohe, H. Takahashi, S. Uemura and N. Sugita, J. Org. Chem., 52 (1987) 4859; A. Toshimitsu, K. Terao and S. Uemura, ibid., 52 (1987) 2018 and ref. therein.
8 Preliminary communication: H. Takahashi, K. Ohe, S. Uemura and N. Sugita, J. Organomet. Chem., 334 (1987) C43.
9 R.F. Heck and D.S. Breslow, J. Am. Chem. Soc., 84 (1962) 2499.
10 C. Screttas and A.F. Isbell, J. Org. Chem., 27 (1962) 2573.
11 R.A. Zingaro, B.H. Steeves and K.J. Irgolic, J. Organomet. Chem., 4 (1965) 320.
12 F. Räuchle, W. Pohl, B. Blaich and J. Goubeau, Ber. Bunsenges. Phys. Chem., 75 (1971) 66.
13 D.L. Klayman and T.S. Griffin, J. Am. Chem. Soc., 95 (1973) 197.
14 J.W. Lewicki, W.H.H. Günther and J.Y.C. Chu, J. Org. Chem., 43 (1978) 2672.
15 W.S. Haller and K.J. Irgolic, J. Organomet. Chem., 38 (1972) 97.
16 N. Petragnani, Tetrahedron, 11 (1960) 15.
17 H. Böhme and H. Schran, Ber., 82 (1949) 453.
18 S.A. Gardner and H.J. Gysling, J. Organomet. Chem., 197 (1980) 111.
19 F.N. Alquist and R.E. Nelson, J. Am. Chem. Soc., 53 (1931) 4033.
20 E.P. Painter, K.W. Franke and R.A. Gortner, J. Org. Chem., 5 (1940) 579.
21 G.H. Denison and P.C. Condit, U.S. Pat 2398415; Chem. Abstr., 40 (1946) 3598.
22 K. Ohe, H. Takahashi, S. Uemura and N. Sugita, Nippon Kagaku Kaishi, (1987) 1469.
23 K.B. Sharpless and M.W. Young, J. Org. Chem., 40 (1975) 947.
24 We followed the method of preparation of similar diselenides: E. Rebane, Arkiv Kemi., 25 (1966) 363; Chem. Abstr., 65 (1966) 8748h.