Some Unusual Reactions of 1,2-Bis(phenylethynyl)benzene with Sulfur, Carbon Monoxide and Alkyl Acetylenedicarboxylates

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1,2-Bis(phenylethynyl)benzene (**1**) reacts with sulfur, carbon monoxide, and acetylenedicarboxylic esters to give unusual polycyclic products. Under exclusion of air **1** adds sulfur to give 6-phenylbenz[*b*]indeno[2,1-*d*]thiopyran (**3b**) and bis(6-phenylbenz[*b*]indeno[2,1-*d*]thiopyran-11-yl) disulfide (**4**). In the presence of air 3-benzoyl-2-phenyl-1*H*-inden-1-one (**5**) is formed via a sulfur-containing intermediate. Under phase-transfer conditions $[CH_3N(C_8H_{17})_3]^+[RhCl_4(H_2O)_2]^-$ promotes reductive carbonylation of **1** to give initially the lactones 3,8-dihydro- and 8,8a-dihydro-3-phenyl-8-(phenylmethylene)-2*H*-indeno[2,1-b]furan-2-one (**6** and **7**) which isomerize to 3-phenyl-8-(phenylmethyl)-2*H*-indeno[2,1-*b*]furan-2-one (**8**). Interaction of **1** and $MeO_2CC{\equiv}CCO_2Me$ in the presence of the same rhodium catalyst results in crosscyclooligomerization in which tetramethyl 2-(phenylethynyl)-1,1′:2′,1″-terphenyl-3′,4′,5′,6′-tetracarboxylate (**9**) is obtained. The H_2PtCl_6-Aliquat-336 catalyst promotes the reaction of **1** with equimolar amounts of $RO_2CC{\equiv}CCO_2R$ (R = Me, Et, Pr) to give the corresponding (*Z*)-2-(10-phenylindeno[2,1-*a*]inden-5-yl)-2-butendioates (**11a–c**). The structures of **3b**, **4**, **5**, **8**, and **11a** have been determined by X-ray diffraction analyses. Possible routes for the transformation of **1** into the polycyclic products are discussed.

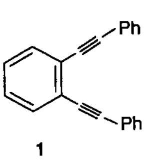
The ability of diynes to undergo intra- and intermolecular [2 + 2 + 2] cycloaddition reactions makes these compounds attractive starting materials for numerous condensed polycycles[1]. Of particular interest are acetylenes with terminal phenyl groups. These groups often participate in building the skeletons of the products as they can turn into *o*-phenylene moieties[2,3]. The reactivity of the phenylated diynes proved to vary greatly in accordance with the proximity of the two carbon–carbon triple bonds. While some phenylated diynes form cyclic products just by brief heating[1c,4], others require the presence of either catalytic[3] or equimolar quantities of a metal complex. (See e.g., the extensive studies of Müller in this area[1c].) 1,2-Bis(phenylethynyl)benzene (**1**) seems to be one of the least reactive diphenylated acetylenes. Although it can be converted by some transition metal salts into 5-phenylindeno[2,1-*a*]indene (**2**)[3–5] and undergoes various photochemical transformations[6], it is thermally stable and unaffected by the $RhCl_3$-Aliquat-336 catalyst[3]. Furthermore, its 1:1 complex with $RhCl(PPh_3)_3$ is also rather infertile. Though it could be hydrogenated[7], it proved refractory (in contrast to other analogous complexes) towards chalcogens and towards organic dienophiles[1c].

We now report the conditions under which **1** reacts in unusual ways with sulfur, carbon monoxide, and active acetylenes to give new carbo- and heteropolycyclic compounds.

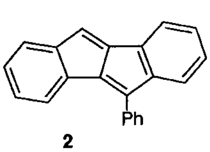
Results and Discussion

Reactions of 1 with Sulfur

The previously reported rearrangement of **1** to **2** by the H_2PtCl_6-Aliquat-336 catalyst[3] was found to be totally inhibited upon addition of sulfur. When, however, sulfur was added in the presence of the $RhCl_3$-Aliquat-336 system[8], two sulfur-containing polycycles – 6-phenylbenz[*b*]indeno[2,1-*d*]-thiopyran (**3b**) and bis(6-phenylbenz[*b*]indeno[2,1-*d*]-thiopyran-11-yl) disulfide (**4**) – were obtained. Thus, e.g. a mixture of **1**, a five-fold excess of sulfur, and some of the rhodium catalyst in 1,1,2,2-tetrachloroethane under argon at 120°C yielded after 18 h 30% of **3b** and 24% of **4**. The product ratio could be adjusted by changing the relative amount of sulfur. In fact, the rhodium compound in this process was found to have only a marginal effect on the rate, and the two sulfur-containing products could be obtained



1



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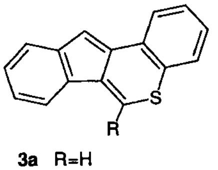
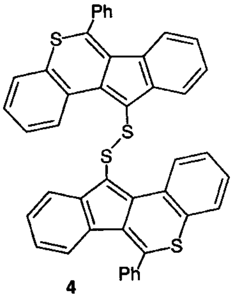


3a R=H
3b R=Ph



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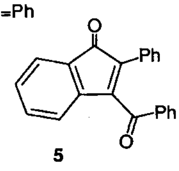

5

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even in complete absence of the metal catalyst. The structures of both **3b** and **4** (which could be separated by column chromatography) were unequivocally determined by X-ray diffraction analyses (see Figures 1 and 2). The UV spectrum of **3b** was shown to resemble closely the spectrum of the unsubstituted parent compound **3a**[9] (Table 1). In the ^{1}H-NMR spectrum of **4** the signals of 1-H and 1′-H appear as a dd at very low field (δ = 9.32). This is explained by the short distances between C1 and S12′ and between C1′ and S12 and by the resulting steric hindrance. The X-ray data reveal that, if H1 and H1′ were placed on the lines that connect C1 with S12′ and C1′ with S12, the corresponding calculated distances H1−S12′ and H1′−S12 would be 2.53 ± 0.01 Å which is shorter than the sum of the van der Waals radii of a hydrogen and a sulfur atom (3.05 Å).

In the *presence of air* the main product proved to be the sulfur-free 3-benzoyl-2-phenyl-1*H*-inden-1-one (**5**) (Figure 3). This compound was occasionally accompanied by small amounts (up to 2%) of **3b**.

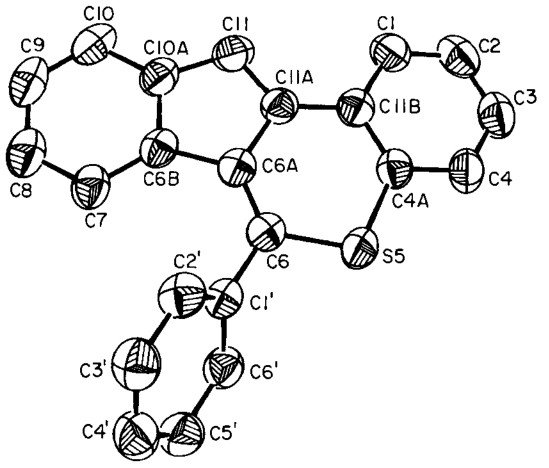


Figure 1. ORTEP drawing of **3b**; selected bond lengths [Å] and angles [°] (with esd's in parentheses): C4a−S5 1.739(2), C4a−C11b 1.399(3), S5−C6 1.729(2), C6−C6a 1.350(3), C6−C1′ 1.476(3), C6a−C6b 1.473(3), C6a−C11a 1.462(2), C6b−C10a 1.406(3), C10a−C11 1.446(3), C11−C11a 1.454(3), C11a−C11b 1.454(3); C4a−S5−C6 104.8(1), S5−C6−C6a 123.0(2), S5−C6−C1′ 111.4(2), C6a−C6−C1′ 125.6(2), C6−C6a−C6b 129.3(2), C6a−C6b−C7 133.7(2), C10−C10a−C11 130.5(3), C11−C11a−C11b 128.2(3), C1−C11b−C11a 120.6(2)

Formally, **3b** can be regarded as the product of sulfur insertion into a five-membered ring of 5-phenylindeno[2,1-*a*]indene (**2**). However, all attempts to convert the latter compound into **3b** by heating of **2** with sulfur failed. We have shown that although S_8 gives sulfur and polysulfide radicals[10], the formation of **3b** and **4** is neither affected by free-radical initiators (verdazyl, benzoyl peroxide), nor by a free-radical scavanger (2,6-di-*tert*-butylhydroquinone). It seems that the key intermediate in the reaction is an adduct of

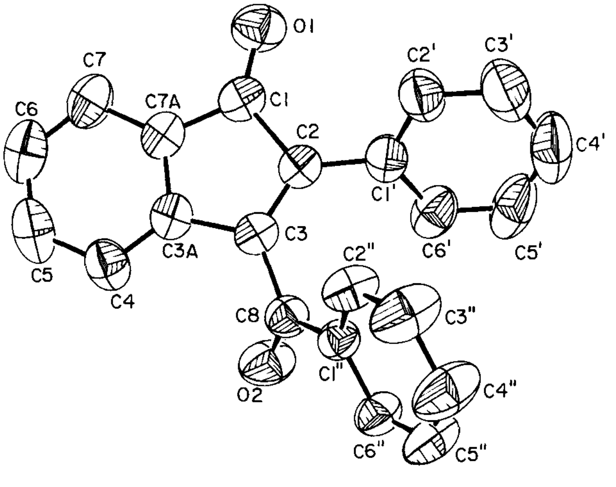


Figure 3. ORTEP drawing of **5**

Table 1. Electronic spectra of benz[*b*]indeno[2,1-*d*]thiopyran (**3a**) and 5-phenylbenz[*b*]indeno[2,1-*d*]thiopyran (**3b**) in heptane

	λ_{max} [nm][a)] (lg ε)								
3a[8]	248.5 (4.09)	284 (infl.) (4.58)	292 (4.75)	313.5 (4.07)		342.4 (4.01)	358.5 (3.87)	364 (3.89)	427 (3.63)
3b	247 (4.41)	280 (infl.) (4.34)	291 (4.62)	315 (4.20)	337 (4.14)	344 (4.15)	356 (infl.) (4.04)	365 (3.98)	436 (3.73)

a) infl.: inflection point.

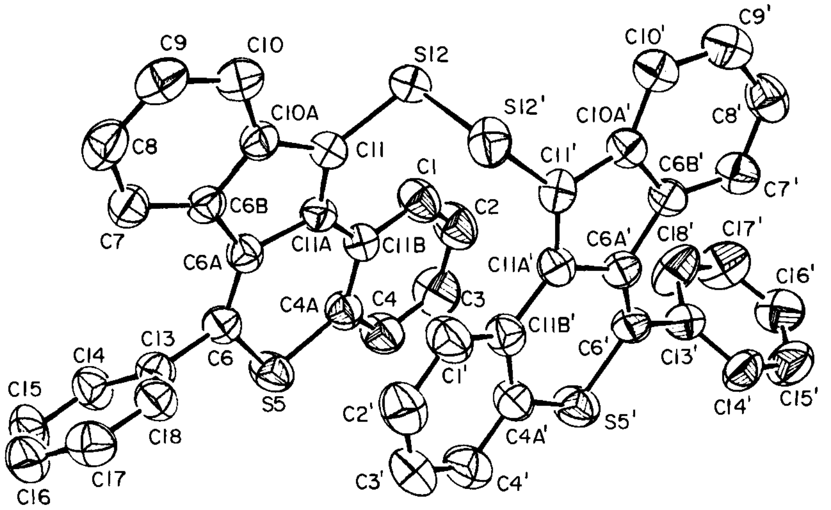
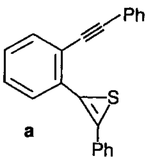
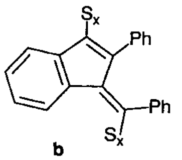


Figure 2. ORTEP drawing of **4**; selected bond lengths [Å] and angles [°] (with esd's in parentheses): C4a−S5 1.757(5), C4a−C11b 1.411(6), S5−C6 1.731(4), C6−C6a 1.362(6), C6−C13 1.488(6), C6−C6b 1.462(5), C6a−C11a 1.487(6), C6b−C10a 1.413(6), C10a−C11 1.458(6), C11−C11a 1.385(5), C11−S12 1.767(4), C11a−C11b 1.453(5), S12−S12′ 2.103(2); C10a−C11−S12 120.1(3), C11a−C11−S12 130.2(3), C11−S12−S12′ 102.6(2), C10a′−C11′−S12 119.8(3), C11a′−C11−S12′ 130.9(3), S12−S12′−C11′ 103.7(2)

sulfur to the carbon–carbon triple bond (**a**) which is similar to those formed from sulfur and some monoalkynes[11]. It is noteworthy that although two hydrogen atoms are eliminated during the formation of **4**, we did not observe the evolution of any H_2S during the process. We assume that the entire hydrogen has been incorporated in the resulting polysulfides.



a

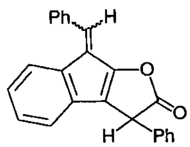


b

Since compound **5** is not formed in the absence of sulfur, we conclude that the diketone results from aerial oxidation of a sulfur-containing intermediate. A possible mechanism may include the reaction of species **a** with sulfur or with polysulfide followed by intramolecular cyclization to **b**, insertion of dioxygen into C–S and S′–S bonds, and cleavage of the resulting C(O)–SO linkages. Support of this pathway is provided by the observation that the formation of **5** is accompanied by continuous evolution of SO_2. The possibility that the carbonyl oxygen atoms in **5** result from water which may be present in the reaction mixture[3] could be excluded on the basis of labelling experiments with $H_2{}^{18}O$ which gave only an ^{18}O-free product.

Reactions of 1 with Carbon Monoxide

Under phase-transfer conditions at 120°C and 48 atm of CO the $RhCl_3$-Aliquat-336 catalyst was found to promote the reductive carbonylation of **1**. At the early stages of the process a mixture of isomers of 3,8-dihydro- and 8,8a-dihydro-3-phenyl-8-(phenylmethylene)-2*H*-indeno[2,1-*b*]furan-2-one (**6** and **7**) were the main products. When the reaction proceeded these compounds (and in particular the highly strained lactone **7**) were gradually transformed into the thermodynamically more stable 3-phenyl-8-(phenylmethyl)-2*H*-indeno[2,1-*b*]furan-2-one (**8**). Thus, e.g., when the carbonylation of **1** was terminated after 36 h we isolated 40% of a mixture of **6** and **7** (7:1) and 17% of pure **8**. At no stage of the reaction did the accumulation of **7** exceed 6%.



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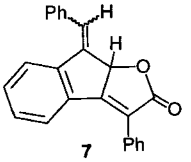

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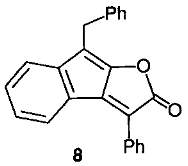

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While the structure of **8** was elucidated by single-crystal X-ray diffraction analysis (see Figure 4), the structures of **6** and **7** (which were difficult to separate) were deduced from their elemental analyses and spectral data. The indicative IR bands of **6** and **7** were the β,γ- and α,β-unsaturated γ-lactone carbonyl peaks at $\tilde{\nu}$ = 1815 and 1760 cm^{-1}. In the ^{1}H-NMR spectrum of the mixture of **6** and **7** appeared singlets of 3-H (**6**) and 8a-H (**7**) at δ = 4.325 and 5.263, and singlets of the vinylic protons at δ = 8.047 and 8.187. In contrast to the 70-eV mass spectrum of **8** (see Experimental) the fragment $(M - CO)^{\cdot +}$ (*m/z* = 308; 40%) and $(M - CHO)^+$ (*m/z* = 307; 100%) dominate the corresponding spectrum of **6** + **7**.

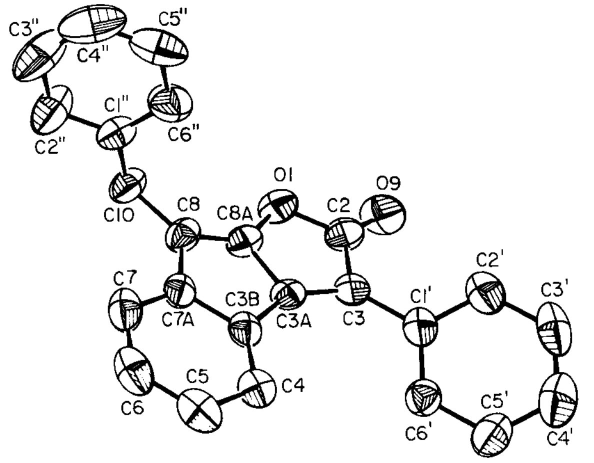
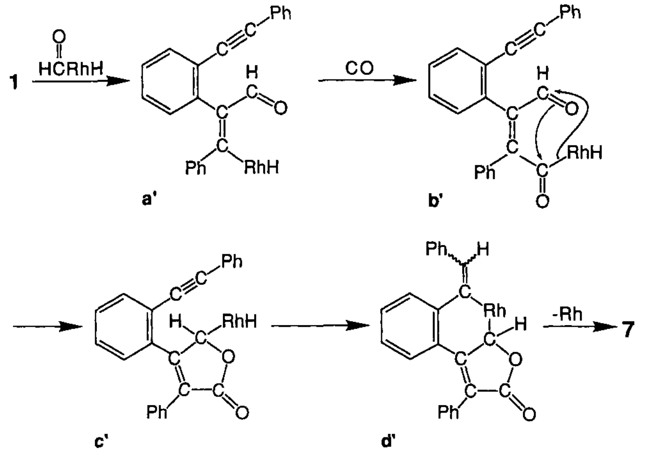


Figure 4. ORTEP drawing of **8**; selected bond lengths [Å] and angles [°] (with esd's in parentheses): O1–C2 1.403(4), O1–C8a 1.381(4), C2–C3 1.485(5), C2–O9 1.196(5), C3–C3a 1.353(4), C3–C1′ 1.467(4), C3a–C3b 1.467(4), C3a–C8a 1.443(4), C3b–C7a 1.430(4), C7a–C8 1.496(5), C8–C8a 1.329(5), C8–C10 1.499(4), C10–C1″ 1.517(5); C2–O1–C8a 105.3(3), O1–C2–C3 109.5(3), O1–C2–O9 119.9(3), C3–C2–O9 130.7(3), C2–C3–C3a 106.0(3), C2–C3–C1′ 122.7(3), C3a–C3–C1′ 131.2(3), C3–C3a–C3b 146.1(3), C3–C3a–C8a 108.1(3), C3b–C3a–C8a 105.6(3), C3a–C3b–C4 134.1(3), C3a–C3b–C7a 105.4(3), C7a–C8–C8a 104.5(3), C7a–C8–C10 125.1(3), C8a–C8–C10 130.4(3), O1–C8a–C3a 111.0(3), O1–C8a–C8 134.4(3), C3a–C8a–C8 114.4(3), C8–C10–C1″ 113.7(3)

The formation of **6** from **1** may be explained in terms of double carbonylation coupled with a hydrogenation reaction. The required hydrogen results from a rhodium-mediated water-gas shift process that takes place under the described experimental conditions (cf., e.g. ref.[12]). A plausible mechanism which is also in line with the reductive carbonylation of monoalkynes[1a] is outlined in an abbreviated form in Scheme 1. The mechanism includes the initial formation of a formylrhodium hydride complex that may add to one of the triple bonds of **1** to form species **a′**. Further addition of CO, followed by intramolecular ring closure, rearrangement, and reductive elimination, can lead to the two stereoisomers of **7**[13]. Since the $RhCl_3$-Aliquat-336 catalyst has already been shown to promote isomerization of allylic compounds[8], the conversion of **7** into **6** and **8** (as well as the transformation of **6** into **8**) is understandable.

Upon replacement of the rhodium catalyst by the analogous H_2PtCl_6-Aliquat-336 system[3], we obtained a complex mixture of products that contained much polymeric material.

Scheme 1



Unspecified ligands are not shown.

Reactions of 1 with Acetylenedicarboxylates

Although the ion pair $[CH_3N(C_8H_{17})_3]^+[RhCl_4(H_2O)_2]^-$ was shown to promote neither intra- nor intermolecular cyclooligomerization of **1**[3], we have now found that under phase-transfer conditions at 104°C the catalyst promotes crosscyclooligomerization of **1** and two equivalents of $MeO_2CC{\equiv}CCO_2Me$ to give tetramethyl 2-(phenylethynyl)-1,1′:2′,1″-terphenyl-3′,4′,5′,6′-tetracarboxylate (**9**). The reaction proved to be rather slow so that much of the dimethyl acetylenedicarboxylate had time to undergo autocyclotrimerization to form hexamethyl benzenehexacarboxylate[2]. Under similar experimental conditions, the H_2PtCl_6-Aliquat-336 catalyst led to a much faster reaction in which a separable mixture of **2** and of an adduct of **1** and dimethyl acetylenedicarboxylate was obtained. On the basis of the molecular weight ($M^{\bullet +}$; *m*/*z* = 420), the ^{1}H-NMR spectrum [δ = 3.842 (s, 3H), 3.888 (s, 3H), 6.421 (s, 1H)], the elemental analysis, and the fact that sulfur forms the benz[*b*]indeno[2,1-*d*]thiopyran derivatives **3b** and **4**, we assumed that this adduct is dimethyl 7-phenyldibenz[*a*,*e*]azulene-5,6-dicarboxylate (**10**, R = Me). However, the UV absorption bands at λ_{max} = 258, 269, 302, and 436 nm (see Table 2) could not be explained in terms of a dibenz[*a*,*c*]azulene derivative[14]. X-ray diffraction analysis showed indeed that the product was not **10**; it was dimethyl (*Z*)-2-(10-phenylindeno-[2,1-*a*]inden-5-yl)-2-butendioate (**11a**) instead (Figure 5). Like $MeO_2CC{\equiv}CCO_2Me$ the corresponding diethyl and dipropyl esters were treated with **1** to give compounds with UV and EI-mass spectra similar to those of **11a** (see Tables 2 and 3). Thus, we conclude that the respective structures of these products are **11b** and **11c**. Although compounds **11a**–**11c** can formally be regarded as the products of an ene addition of **2** to $RO_2CC{\equiv}CCO_2R$[5], we found that no reaction takes place when **1** is replaced by **2** as starting material. Since various free-radical initiators proved to stop rather than to promote the formation of the 2-(10-phenylindeno[2,1-*a*]inden-5-yl)-2-butendioates, it is unlikely that the addition process described here involves free-radical intermediates. We propose that the mechanism involves the initial reduction of the Pt^{IV} compound and formation of a (π-alkyne)platinum(II) complex **a″**. This species may rearrange to give a series of metallacyclic species **b″**–**d″** and a plati-

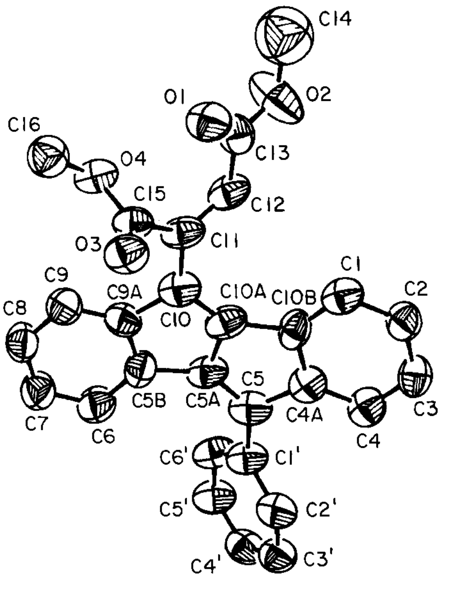


Figure 5. ORTEP drawing of **11a**; selected bond lenths [Å] and angles [°] (with esd's in parentheses): C4a–C5 1.521(9), C4a–C11b 1.418(7), C5–C5a 1.321(9), C5–C1′ 1.468(7), C5a–C5b 1.50(1), C5a–C10a 1.437(7), C5b–C9a 1.406(7), C9a–C10 1.524(9), C10–C10a 1.328(9), C10–C11 1.478(7), C10a–C10b 1.51(1), C11–C12 1.327(9), C11–C15 1.471(8), C12–C13 1.488(7); C4a–C5–C1′ 126.9(5), C5a–C5–C1′ 128.8(6), C9a–C10–C11 127.1(5), C10a–C10–C11 127.4(6), C10–C11–C12 122.7(6), C10–C11–C15 117.0(5), C12–C11–C15 120.3(7), C11–C12–C13 124.2(6)

Table 2. Ultraviolet spectra of compounds **11a**–**11c**[a]

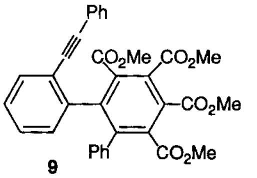
	λ_{max} [nm][b] (lg ε)					
11a		258 (4.53)		269 (4.52)	302 (infl.) (4.25)	436 (3.93)
11b		257 (4.48)	264 (4.49)	268 (4.48)	302 (infl.) (4.24)	435 (3.94)
11c	237 (4.67)	254 (4.66)		268 (infl.) (4.63)	302 (infl.) (4.32)	435 (3.99)

[a] In THF. – [b] infl.: inflection point.

Table 3. EI mass spectra of compounds **11a**–**11c**[a]

	11a	**11b** *m*/*z* (%)[b]	**11c**
$M^{\bullet +}$	420 (100)	448 (100)	476 (100)
$(M - OR)^+$	389 (4)	403 (4)	417 (3)
$(M - COOR)^+$	361 (14)	375 (7)	389 (3)
$C_{25}H_{16}O_2^{\bullet +}$	348 (4)	348 (14)	348 (15)
$C_{25}H_{15}O_2^+$	347 (12)	347 (7)	347 (4)
$C_{24}H_{15}^+$	303 (31)	303 (40)	303 (45)
$C_{24}H_{13}^+$	301 (21)	301 (16)	301 (17)
$C_{23}H_{14}^{\bullet +}$	290 (6)	290 (7)	290 (5)
$C_{22}H_{13}^+$	277 (4)	277 (5)	277 (4)

[a] Ionization energy: 70 eV; ionization temperatures: 130, 140, or 250°C for **11a, 11b,** or **11c**. – [b] The data given are corrected for natural ^{13}C contributions.



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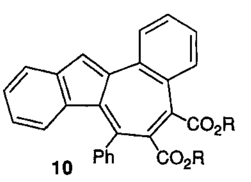

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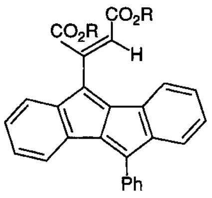
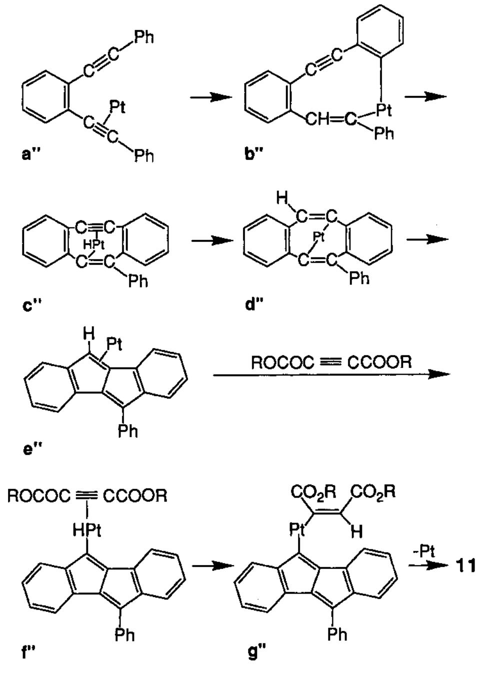


11a R=Me
11b R=Et
11c R=Pr

num derivative of 5-phenylindeno[2,1-*a*]indene (**2**). Since we were unable to trace the fate of the chlorine ligands during these transformations, the latter compound may be either a π complex (as in **e″**) or a σ compound in which the metal is bound to C-10. Reaction of either of these compounds with the active dialkyl acetylenedicarboxylate is likely to give a π complex **f″**. The product **11** could then be formed by intramolecular hydrogen transfer, followed by a reductive elimination process (Scheme 2).

Scheme 2



Unspecified ligands are not shown.

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Experimental

General: Melting points (not corrected): Thomas-Hoover capillary melting point apparatus. – IR: Perkin-Elmer Model 457. – UV: UVICON 860. – ^{1}H and ^{13}C NMR: Bruker WP 200 SY and AMX 400. – MS: Varian MAT-311. -- Elemental analyses: Perkin-Elmer CHN Analyzer Model 240C.

Reaction of Bis(phenylethynyl)benzene (**1**) *with Sulfur:* In a typical experiment a mixture of 556 mg (2 mmol) of **1**, 10 ml of $(CHCl_2)_2$ and 320 mg (10 mmol) of sulfur was stirred under argon at 120°C until the entire diyne had been consumed (18 h). The resulting mixture was chromatographed on silica gel using a 1:9 mixture of ether/hexane as eluent. The two first fractions consisted of 186 mg (30%) of 6-phenylbenz[*b*]indeno[2,1-*d*]thiopyran (**3b**) and 164 mg (24%) of disulfide **4**.

3b: R_f = 0.65; ruby-red crystals, m.p. 136.1–136.5°C (from hexane). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.833 (d, J = 7.8 Hz, 1 H, 4- or 7-H), 6.975 (dd, J_1 = J_2 = 7.5 Hz, 1 H), 7.290–7.581 (m, 11 H), 8.263 (d, J = 8 Hz, 1 H, 1-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 116.08, 120.14, 122.52, 122.84, 125.41, 125.50, 126.44, 126.84, 127.38, 128.07, 129.08, 129.13, 129.38, 129.62, 129.72, 130.79, 130.96, 136.57, 140.61, 141.85. – EI MS (70 eV, 75°C): *m/z* (%) = 310 (100) [$M^{\bullet +}$], 308 (17) [$C_{22}H_{12}S^{\bullet +}$], 202 (17) [$C_{16}H_{10}^{\bullet +}$].

$C_{22}H_{14}S$ (310.4) Calcd. C 85.12 H 4.55 S 10.33
Found C 84.92 H 4.37 S 10.09

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from a 1:9 mixture of ether/hexane. The unit cell was found to consist of two independent molecules. Details of the crystal data, the experimental conditions and a summary of the solution and refinement are given in Table 4. The positional coordinates and equivalent isotropic thermal parameters for one of the molecules in the unit cell are listed in Table 5. An ORTEP drawing of **3b** is shown as Figure 1[16].

4: R_f = 0.45; dark red crystals, m.p. 246.6–247.6°C (from $CHCl_3$). – ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 6.463 (dd, J_1 = 0.8 Hz, J_2 = 7.8 Hz, 2 H, 7-, 7′-H), 6.530 (dt, J_d = 1.4 Hz, J_t = 7.1 Hz, 2 H, 2-, 2′-H), 6.970 (dt, J_d = 1.1 Hz, J_t = 8.1 Hz, 2 H, 8-, 8′-H), 7.085 (dt, J_d = 1.3 Hz, J_t = 7.2 Hz, 2 H, 3-, 3′-H), 7.303–7.606 (m, 14 H), 7.935 (d, J = 7.8 Hz, 2 H, 10-, 10′-H), 9.324 (dd, J_1 = 1.0 Hz, J_2 = 8.5 Hz, 2 H, 1-, 1′-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 119.40, 120.82, 121.97, 123.53, 124.56, 125.99, 126.15, 125.76, 127.73, 127.91, 128.83, 128.96, 129.02, 129.70, 129.88, 129.97, 135.97, 136.46, 141.79, 143.02. – EI MS (70 eV, 190°C): *m/z* (%) = 342 (48) [$C_{22}H_{14}S_2^{\bullet +}$], 310 (100) [$C_{22}H_{14}S^{\bullet +}$], 308 (24) [$C_{22}H_{12}S^{\bullet +}$].

$C_{44}H_{26}S_4$ (683.0) Calcd. C 77.38 H 3.84
Found C 77.05 H 4.14

A crystal for structure determination was obtained by slow recrystallization from hexane. The crystallographic details are given in Table 4. Positional coordinates are listed in Table 6. An ORTEP drawing of **4** is shown as Figure 2[16].

3-Benzoyl-2-phenyl-1H-inden-1-one (**5**): When the above reaction of **1** and sulfur was conducted under air 351 mg (56%) of **5** and 12 mg (2%) of **3b** were obtained.

5: R_f (silica gel; 1:9 ether/hexane mixture as eluent) = 0.24; yellow crystals, m.p. 125.8–127.2°C (from hexane). – IR ($CHCl_3$): $\tilde{\nu}$ = 1715 cm^{-1} (cyclic C=O), 1650 (C=O). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.028 (d, J = 7.2 Hz, 1 H, 4-H), 7.200–7.422 (m, 9 H), 7.492 (tt, J_1 = 0.9 Hz, J_2 = 7.4 Hz, 1 H, 4- or 4″-H), 7.606 (d, J = 7.1 Hz, 1 H, 7-H), 7.909 (dd, J_1 = 1.3 Hz, J_2 = 8.2 Hz, 2 H, 2″-, 6″-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 121.74, 123.85, 128.27, 128.78, 128.94, 129.31, 129.32, 129.33, 129.54, 129.66, 134.34, 134.37, 134.62, 135.15, 144.05, 150.36, 194.54, 195.97. – EI MS (70 eV, 110°C): *m/z* (%) = 310 (100) [$M^{\bullet +}$], 281 (44) [$C_{21}H_{13}O^+$], 253 (20) [$C_{20}H_{13}^+$], 205 (24) [$C_{15}H_9O^+$], 276 (53) [$C_{14}H_8^{\bullet +}$].

$C_{22}H_{14}O_2$ (310.4) Calcd. C 85.14 H 4.55
Found C 85.04 H 4.80

Table 4. Crystal data and details of structure determination for **3b**, **4**, **5**, **8**, and **11a**[16,17]

	3b	**4**	**5**	**8**	**11a**
Emp. formula	$C_{22}H_{14}S$	$C_{44}H_{26}S_4$	$C_{22}H_{14}O_2$	$C_{24}H_{16}O_2$	$C_{28}H_{20}O_4$
Formula weight	310.4	683.0	310.4	336.4	420.5
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	I2/c	C2/c
a, [Å][a)]	12.489(4)	12.588(3)	19.686(4)	23.499(5)	20.478(6)
b, [Å]	13.822(4)	13.827(3)	10.118(2)	7.359(2)	8.271(4)
c, [Å]	9.827(2)	10.034(2)	8.525(1)	20.207(4)	26.764(6)
α, [°]	107.25(2)	94.34(2)			
β, [°]	96.97(2)	108.28(2)	96.65(2)	95.73(2)	109.84(3)
γ, [°]	98.65(2)	87.27(2)			
V, [$Å^3$]	1583.9(7)	1653.0(5)	1687.5(5)	3476.9(7)	4264(1)
Z	4	2	4	8	8
ρ(calc.),[g cm^{-3}]	1.30	1.37	1.22	1.29	1.31
μ [cm^{-1}]	(CuK_α) 16.53	(MoK_α) 2.72	(MoK_α) 0.43	(MoK_α) 0.44	(CuK_α) 6.18
Diffraction	Enraf-Nonius CAD-4	PW1100/20	PW1100/20	PW1100/20	Enraf-Nonius CAD-4
Radiation, [Å]	1.54178	0.71069	0.71069	0.71069	1.54178
Scanning technique	θ-2θ	ω-2θ	ω-2θ	ω-2θ	θ-2θ
2θ, min, max [°]	3-110	3-45	3-50	3-50	3-110
Scan width, [°]	0.80+0.15 tan θ	1.00+0.35 tan θ	1.00+0.35 tan θ	1.00+0.35 tan θ	0.80+0.15 tan θ
No. of unique reflections	3853	4239	2880	2550	2511
No. of observed reflections	3568	2806	1830	1690	2060
	$I \geqslant 3\sigma(I)$	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
R[b)]	0.040	0.043	0.052	0.053	0.085
R_w[c)]	0.067	0.052	0.060	0.064	0.104
w^{-1}	$\sigma(F)^2$	$\sigma(F)^2$	$\sigma(F)^2+0.000296F^2$	$\sigma(F)^2+0.000718F^2$	$\sigma(F)^2$

[a)] Cell dimensions were determined by least-squares fit of the setting angles of 18–20 reflections with 2Θ in the range of 21–28° for **3b**, 10–12° for **4**, 10–14° for **5**, 10–13° for **8**, and 20–28° for **11a**. – [b)] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. – [c)] $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w(| F_o |)^2]^{1/2}$.

Table 5. Fractional atomic coordinates (× 10^4) and equivalent isotropic parameters (× 10^3)[a)] for one of the molecules of **3b** in the unit cell with esd's in parentheses[16]

Atom	*x*	*y*	*z*	*U*[$Å^2$]
C1	4158(2)	935(2)	-1848(3)	63(1)
C2	3213(2)	1091(2)	-2571(3)	70(2)
C3	3026(2)	2081(2)	-2375(3)	71(2)
C4	3767(2)	2902(2)	-1435(3)	67(2)
C4a	4731(2)	2757(2)	-690(2)	54(2)
S5	5597.8(5)	3877.3(4)	469.9(7)	63(1)
C6	6716(2)	3462(2)	1161(2)	49(1)
C6a	6806(2)	2459(2)	786(2)	50(1)
C6b	7742(2)	1999(2)	1167(2)	52(1)
C7	8817(2)	2410(2)	1901(2)	59(1)
C8	9529(2)	1760(2)	1979(3)	70(2)
C9	9204(2)	707(2)	1352(3)	77(2)
C10	8157(2)	271(2)	608(3)	73(2)
C10a	7413(2)	925(2)	503(2)	59(1)
C11	6308(2)	697(2)	-304(2)	60(1)
C11a	5951(2)	1606(2)	-170(2)	51(1)
C11b	4938(2)	1761(2)	-895(2)	52(1)
C1'	7525(2)	4334(2)	2204(2)	49(1)
C2'	7788(2)	4389(2)	3641(2)	61(1)
C3'	8564(2)	5202(2)	4599(2)	65(2)
C4'	9083(2)	5971(2)	4136(3)	62(2)
C5'	8803(2)	5936(2)	2714(3)	63(1)
C6'	8031(2)	5130(2)	1757(2)	56(1)

[a)] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

A suitable crystal for X-ray diffraction analysis was obtained from hexane. The crystallographic data are given in Table 4, and an ORTEP drawing is shown as Figure 3[16].

Carbonylation of **1**: A mixture of 70 mg (0.25 mmol) of **1**, 7 mg (2.5 × 10^{-2} mmol) of $RhCl_3 \cdot 3\,H_2O$, 10 mg (2.5 × 10^{-2} mmol) of Aliquat 336, 1 ml of $(CHCl_2)_2$, and 1 ml of H_2O were introduced into a miniautoclave. The apparatus was sealed, purged with argon (20 atm), and charged with 48 atm of CO. The mixture was stirred at 120°C. After 36 h, the autoclave was cooled and opened and its content worked up in the usual manner. Column chromatography on silica gel, with ether/hexane mixtures as eluent, afforded 14 mg (17%) of pure **8** and 34 mg (40%) of a 7:1 mixture of **6** and **7**.

6 + **7**: R_f [ether/hexane (1:9)] = 0.29; pale yellow crystals, m.p. 128–129°C (from a 1:1 mixture of ether/hexane). – IR ($CHCl_3$): $\tilde{\nu}$ = 1815 cm^{-1} (C=O of **6**), 1760 (C=O of **7**). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.325 (s, 0.12 H), 5.263 (s, 0.88 H), 7.257–7.540 (m, 11 H), 7.821 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 2 H), 7.940 (dd, J_1 = 1 Hz, J_2 = 8 Hz, 0.88 H), 8.047 (s, 0.88 H), 8.187 (s, 0.12 H). – EI MS (70 eV, 120°C): *m/z* (%) = 336 (63) [$M^{\bullet +}$], 308 (40) [$(M - CO)^{\bullet +}$], 307 (100) [$(M - CHO)^+$], 279 (9) [$C_{22}H_{15}^+$], 278 (10) [$C_{22}H_{14}^{\bullet +}$], 277 (10) [$C_{22}H_{13}^+$], 276 (15) [$C_{22}H_{12}^{\bullet +}$], 203 (11) [$C_{16}H_{11}^+$], 202 (28) [$C_{16}H_{10}^{\bullet +}$].

$C_{24}H_{16}O_2$ (336.4) Calcd. C 85.69 H 4.79
Found C 85.65 H 4.58

8: R_f [ether/hexane (1:9)] = 0.44; orange crystals, m.p. 120–121°C (from CH_2Cl_2 and hexane). – IR ($CHCl_3$): $\tilde{\nu}$ = 1765 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.825 (s, 2H, CH_2), 6.900 (dd, J_1 = 1.0 Hz, J_2 = 7.3 Hz, 1H, 4- or 7-H); 6.958 (m, 1H, 5- or 6-H), 7.130 (m, 1H, 5- or 6-H), 7.220–7.353 (m, 5H, 2″-, 3″-, 4″-, 5″-, 6″-H), 7.442–7.540 (m, 3H, 3′-, 4′-, 5′-H), 7.573 (dd, J_1 = 1.0 Hz, J_2 = 8.2 Hz, 1H, 4- or 7-H), 7.868 (dd, J_1 = 1.6 Hz, J_2 = 8.6 Hz, 2H, 2′-, 6′-H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 30.92, 116.43, 121.13, 124.65, 125.72; 126.74, 127.56, 128.69, 128.71, 128.74, 128.86, 129.29, 129.61, 129.96, 131.84, 137.12, 146.91, 149.29, 151.52, 171.41. – EI MS (70 eV, 120°C): *m/z* (%) =

Table 6. Fractional atomic coordinates (× 10^4) and equivalent atomic parameters (× 10^3)[a)] for **4** with esd's in parentheses[16]

Atom	*x*	*y*	*z*	*U*[Å^2]
C1	2227(4)	2289(3)	174(5)	69(3)
C2	2169(4)	1375(4)	-497(5)	73(4)
C3	1230(5)	816(4)	-719(5)	77(4)
C4	360(4)	1192(3)	-281(5)	62(3)
C4a	411(3)	2120(3)	402(4)	50(3)
S5	-7923(9)	24845(8)	859(1)	60.1(8)
C6	-565(3)	3685(3)	1471(4)	45(3)
C6a	395(3)	4148(3)	1587(4)	43(3)
C6b	673(3)	5153(3)	2087(4)	45(3)
C7	36(4)	5969(3)	2330(4)	54(3)
C8	565(4)	6840(3)	2798(5)	66(3)
C9	1719(4)	6915(3)	3044(5)	68(4)
C10	2357(4)	6119(3)	2792(5)	56(3)
C10a	1827(3)	5241(3)	2281(4)	46(3)
C11	2261(3)	4320(3)	1829(4)	47(3)
C11a	1402(3)	3668(3)	1332(4)	43(3)
C11b	1360(3)	2695(3)	664(4)	47(3)
S12	3702.8(9)	4166.7(8)	2026(1)	57.6(8)
C13	-1489(3)	4124(3)	1964(5)	47(3)
C14	-2564(3)	4275(3)	1036(5)	54(3)
C15	-3397(4)	4707(4)	1544(6)	69(4)
C16	-3175(4)	4978(3)	2953(6)	69(4)
C17	-2119(4)	4814(3)	3874(5)	64(3)
C18	-1284(4)	4388(3)	3390(5)	53(3)
C1'	2264(4)	2444(4)	4531(5)	69(3)
C2'	1284(5)	2425(4)	4869(6)	87(4)
C3'	656(4)	1587(6)	4583(6)	88(4)
C4'	1032(4)	774(4)	3980(5)	75(4)
C4a'	2033(4)	782(3)	3628(5)	58(3)
S5'	2391(1)	-318.2(9)	2886(1)	47.6(9)
C6'	3724(3)	-145(3)	2809(4)	49(3)
C6a'	4253(3)	706(3)	3214(4)	45(3)
C6b'	5387(3)	930(3)	3199(4)	44(3)
C7'	6290(4)	346(3)	3050(5)	55(3)
C8'	7277(4)	803(4)	3129(5)	64(3)
C9'	7355(4)	1809(4)	3329(5)	67(3)
C10'	6469(4)	2389(3)	3493(4)	55(3)
C10a'	5488(3)	1943(3)	3456(4)	46(3)
C11'	4471(3)	2360(3)	3682(4)	46(3)
C11a'	3742(3)	1622(3)	3614(4)	45(3)
C11b'	2669(4)	1627(3)	3900(4)	51(3)
S12'	4353(1)	3628.5(8)	4035(1)	55.2(7)
C13'	4165(3)	-1026(3)	2168(4)	47(3)
C14'	4420(4)	-1871(3)	2847(5)	67(3)
C15'	4857(5)	-2667(4)	2246(6)	87(4)
C16'	5038(4)	-2624(4)	978(6)	75(4)
C17'	4759(5)	-1786(4)	274(5)	82(4)
C18'	4319(5)	-994(5)	874(5)	77(4)

[a)] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

336 (100) [$M^{\cdot +}$], 308 (3) [$(M - CO)^{\cdot +}$], 307 [$(M - CHO)^+$], 279 (19) [$C_{22}H_{15}^+$], 278 (16) [$C_{22}H_{14}^{\cdot +}$], 277 (13) [$C_{22}H_{13}^+$], 276 (16) [$C_{22}H_{12}^{\cdot +}$], 231 (15) [$C_{17}H_{10}^+$], 203 (19) [$C_{16}H_{11}^+$], 202 (36) [$C_{16}H_{10}^{\cdot +}$].

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from a mixture of CH_2Cl_2 and hexane. Details of the crystal data are given in Table 4. The positional coordinates are listed in Table 7. An ORTEP drawing of **8** is shown as Figure 4[16].

Table 7. Fractional atomic coordinates (× 10^4) and equivalent isotropic parameters (× 10^3)[a)] for **8** with esd's in parentheses[16]

Atom	*x*	*y*	*z*	*U*[Å^2]
O1	5418(1)	789(3)	3355(1)	61(2)
C2	5973(2)	929(5)	3677(2)	56(2)
C3	5946(1)	1642(4)	4361(2)	44(2)
C3a	5384(1)	1817(4)	4440(2)	43(2)
C3b	4961(1)	2418(4)	4880(2)	44(2)
C4	4992(1)	2987(4)	5531(2)	51(2)
C5	4489(2)	3447(4)	5800(2)	63(2)
C6	3964(2)	3363(5)	5418(2)	67(2)
C7	3929(1)	2833(4)	4752(2)	61(2)
C7a	4421(1)	2337(4)	4485(2)	47(2)
C8	4502(1)	1670(4)	3801(2)	52(2)
C8a	5061(2)	1356(4)	3818(2)	49(2)
O9	6374(1)	493(4)	3392(1)	76(2)
C10	4036(1)	1490(4)	3241(2)	61(2)
C1'	6459(1)	2115(4)	4802(2)	46(2)
C2'	6941(1)	2842(5)	4548(2)	62(2)
C3'	7401(1)	3457(5)	4978(2)	72(2)
C4'	7388(2)	3318(5)	5657(3)	77(3)
C5'	6923(2)	2563(5)	5908(2)	69(2)
C6'	6458(1)	1966(4)	5490(2)	51(2)
C1"	3826(2)	3296(5)	2948(2)	56(2)
C2"	3256(2)	3549(6)	2746(2)	88(3)
C3"	3070(2)	5165(8)	2432(3)	109(4)
C4"	3439(3)	6506(7)	2334(2)	103(4)
C5"	4005(2)	6300(6)	2542(2)	92(3)
C6"	4200(2)	4693(5)	2850(2)	72(3)

[a)] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Reaction of **1** *with* $MeO_2CC{\equiv}CCO_2Me$ *in the Presence of the* $RhCl_3$*-Aliquat-336 Catalyst:* A mixture of 278 mg (1 mmol) of **1**, 142 mg (1 mmol) of $MeO_2CC{\equiv}CCO_2Me$, 26 mg (0.1 mmol) of $RhCl_3 \cdot 3\ H_2O$, 40 mg (0.1 mmol) of Aliquat 336, 2 ml of $(CHCl_2)_2$, and 2 ml of deionized H_2O was stirred at 104°C. After 16 h, the mixture was cooled, the phases were separated, and the organic material was chromatographed on silica gel using pure hexane and hexane/ether mixtures as eluents. A 9:1 hexane/ether mixture eluted 111 mg (40%) of unreacted **1**. A 1:1 mixture of these solvents eluted 69 mg (34% based on consumed **1**) of the tetracarboxylate **9**. – R_f = 0.17; cream-colored crystals, m.p. 117–119°C (from ether/hexane). – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.460 (s, 3H, CH$_3$), 3.490 (s, 3H, CH$_3$), 3.900 (s, 3H, CH$_3$), 3.912 (s, 3H, CH$_3$), 6.956–7.388 (m, 14H, Ar-H). – $^{13}C\{^1H\}$ NMR (CDCl$_3$, 50 MHz): δ = 52.40, 53.07, 53.09, 53.15, 87.78, 94.01, 122.82, 123.12, 127.22, 127.31, 127.55, 127.62, 127.74, 128.27, 129.04, 129.27, 129.93, 130.05, 130.77, 131.23, 131.54, 135.07, 135.82, 136.49, 139.46, 142.12, 166.26, 166.55, 166.60, 167.31. – EI MS (70 eV, 260°C): *m/z* (%) = 562 (10) [$M^{\cdot +}$], 531 (6) [$(M - OCH_3)^+$], 503 (100) [$C_{32}H_{23}O_6^+$], 485 (15) [$C_{28}H_{21}O_8^+$], 457 (7) [$C_{27}H_{21}O_7^+$], 326 (12) [$C_{26}H_{14}^{\cdot +}$].

$C_{34}H_{26}O_8$ (562.6) Calcd. C 72.59 H 4.66
Found C 72.49 H 4.38

Reaction of **1** *with Dialkyl Acetylenedicarboxylates in the Presence of the* H_2PtCl_6*-Aliquat-336 Catalyst:* A mixture of 278 mg (1 mmol) of **1**, 1 mmol of the appropriate dialkyl acetylenedicarboxylate, 25.9 mg (5 × 10^{-2} mmol) of $H_2PtCl_6 \cdot 6\ H_2O$, and 20.2 mg (5 × 10^{-2} mmol) of Aliquat 336 was heated at 104°C for 15–24 h under phase-transfer conditions. The mixture of products was separated by chromatography on silica gel. The first fraction was eluted with a 1:19 mixture of ether/hexane and consisted of 5-phenylindeno[2,1-*a*]indene (**2**)[3] (55, 60, and 51% in the experiments with the dimethyl, diethyl, and dipropyl esters). Compounds **11a**–**11c** were obtained by elution with a 1:9 mixture of the same solvents.

Dimethyl (Z)-2-(10-Phenylindeno[2,1-a]inden-5-yl)-2-butendiolate (**11a**): Yield 151 mg (36%); R_f = 0.10; dark red crystals, m.p. 122–124°C (from acetone). – IR (CHCl$_3$): ṽ = 1719 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.842 (s, 3H, CH$_3$), 3.888 (s, 3H, CH$_3$), 6.421 (s, 1H, C*H*CO$_2$Me), 6.820–7.638 (m, 13H, Ar-H). – $^{13}C\{^1H\}$ NMR (CDCl$_3$, 50 MHz): δ = 52.25, 52.86, 121.96, 122.33, 122.88, 123.41, 124.24, 127.68, 128.12, 128.29, 128.31, 128.69, 129.24, 132.59, 133.17, 133.29, 134.29, 141.63, 142.52, 143.10, 146.89, 148.15, 149.86, 165.05, 166.55.

$C_{28}H_{20}O_4$ (420.5) Calcd. C 79.98 H 4.79
Found C 80.28 H 4.76

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization (3 d) from acetone. Details of the crystal data are given in Table 4. The positional coordinates are listed in Table 8. An ORTEP drawing of **11a** is shown as Figure 5[16].

11b: Yield 138 mg (25%); R_f = 0.18; dark red oil. – IR (CHCl$_3$): ṽ = 1720 cm^{-1} (C=O). – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 1.337

Table 8. Fractional atomic coordinates (× 10^4) and equivalent isotropic parameters (× 10^3)[a] for **11a** with esd's in parentheses[16]

Atom	*x*	*y*	*z*	*U*[Å^2]
O1	1188(2)	6526(5)	2734(2)	76(3)
O2	1372(3)	8674(6)	3253(2)	108(4)
O3	1956(2)	2998(5)	2984(2)	74(3)
O4	2454(2)	5078(5)	2704(1)	70(3)
C1	1934(3)	5715(7)	4770(2)	65(4)
C2	1676(3)	5800(7)	5189(2)	64(4)
C3	2043(3)	5159(8)	5676(2)	70(4)
C4	2686(3)	4431(7)	5772(2)	67(4)
C4a	2961(3)	4325(7)	5372(2)	64(4)
C5	3649(3)	3618(7)	5377(2)	63(4)
C5a	3628(3)	3742(7)	4880(2)	61(4)
C5b	4023(3)	3136(7)	4537(2)	66(4)
C6	4629(3)	2211(8)	4629(2)	73(5)
C7	4802(3)	1738(8)	4192(2)	78(4)
C8	4402(3)	2200(8)	3685(2)	73(4)
C9	3806(3)	3103(7)	3597(2)	65(4)
C9a	3619(3)	3564(7)	4015(2)	60(4)
C10	2977(3)	4484(7)	4022(2)	67(4)
C10a	3015(3)	4509(7)	4527(2)	64(4)
C10b	2580(3)	4947(7)	4863(2)	66(4)
C11	2423(3)	5173(8)	3560(2)	61(4)
C12	2078(3)	6505(8)	3593(2)	64(4)
C13	1501(3)	7199(8)	3142(3)	66(4)
C14	881(5)	9580(10)	2838(4)	158(4)
C15	2242(3)	4276(8)	3057(2)	61(4)
C16	2226(3)	4396(8)	2172(2)	82(2)
C1'	4208(3)	2983(7)	5839(2)	58(4)
C2'	4071(3)	2007(7)	6198(2)	65(4)
C3'	4579(3)	1495(7)	6652(2)	66(4)
C4'	5259(4)	1930(8)	6739(2)	68(5)
C5'	5424(3)	2880(8)	6384(2)	70(4)
C6'	4903(4)	3415(7)	5931(2)	73(4)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

(t, J = 7.1 Hz, 3H, CH_3), 1.354 (t, J = 7.1 Hz, 3H, CH_3), 4.299 (q, J = 7.1 Hz, 2H, CH_2), 4.356 (q, J = 7.1 Hz, 2H, CH_2), 6.397 (s, 1H, $C\textit{H}CO_2Et$), 6.790 – 7.650 (m, 13H, Ar-H).

$C_{30}H_{24}O_4$ (448.5)	Calcd.	C 80.34	H 5.39
	Found	C 80.01	H 5.68

11c: Yield 138 mg (29%); R_f = 0.18; dark red crystals, m.p. 89 – 91 °C (from pentane). – IR ($CHCl_3$): $\tilde{\nu}$ = 1719 cm^{-1} (C=O). – ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.931 (t, J = 7.4 Hz, 3H, CH_3), 0.996 (t, J = 7.4 Hz, 3H, CH_3), 1.764 (m, 4H, $C\textit{H}_2Me$), 4.195 (t, J = 6.8 Hz, 2H, OCH_2), 4.243 (t, J = 6.8 Hz, 2H, OCH_2), 6.408 (s, 1H, $C\textit{H}CO_2Pr$), 6.826 – 7.651 (m, 13H, Ar-H).

$C_{32}H_{28}O_4$ (476.6)	Calcd.	C 80.65	H 5.92
	Found	C 80.38	H 5.93

CAS Registry Numbers

1: 13203-60-6 / **2**: 17261-24-4 / **3b**: 138408-19-2 / **4**: 138408-20-5 / **5**: 72686-15-8 / **6**: 138408-26-1 / **7**: 138408-27-2 / **8**: 138408-24-9 / **9**: 138408-25-0 / **11a**: 138408-21-6 / **11b**: 138408-22-7 / **11c**: 138408-23-8 / $RhCl_3$: 10049-07-7 / $MeO_2CC{\equiv}CCO_2Me$: 762-42-5 / $EtO_2CC{\equiv}CCO_2Et$: 762-21-0 / $PrO_2CC{\equiv}CCO_2Pr$: 14447-02-0 / H_2PtCl_6: 16941-12-1 / sulfur: 7704-34-9 / carbon monoxide: 630-08-0

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