Versatile Bis-Propargylic Reactivity of Acetylenedicarbonyl−Cobalt Complexes with Neutral C-Nucleophiles: Direct Synthesis of a Furyl-α-pyrone

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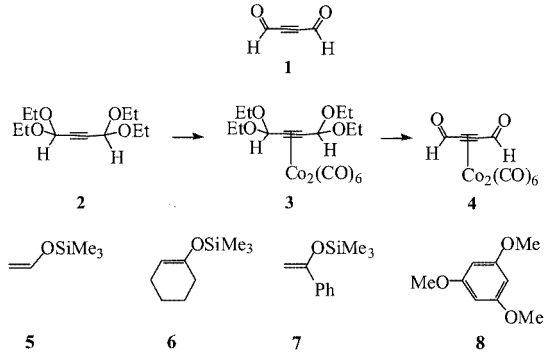
Double aldol reactions of the $Co_2(CO)_6$ complex of acetylenedicarbaldehyde with several enol ethers have been carried out and compared with the double Nicholas reactions of the corresponding bis(diethyl acetal) complex. The selectivity was found to depend on (i) the nucleophile, (ii) the solvent, and (iii) the number of equivalents of the auxiliary $BF_3{\cdot}OEt_2$. While silyl enol ethers give mono- and 1,4-bis-dialkylation products only, trimethoxybenzene affords 1,1-bis- and 1,1,4-tris-arylation products. In dichloromethane as solvent, the trimethylsilyl enol ether of acetophenone exhibits novel behaviour. In this solvent, and in the presence of an excess acid, the primary bis(aldol) product evolves to the $Co_2(CO)_6$ complex of 1-phenyl-4-(5-phenyl-2-furyl)-but-3-yn-1-one and to 3-(5-phenyl-2-furyl)-6-phenyl-2*H*-pyran-2-one. These products are rationalised in terms of a common double aldol–cyclodehydration process, followed by α-slippage of the μ-$Co_2(CO)_6$ unit, and by a cyclocarbonylation–decomplexation process, respectively. Reaction of the trimethylsilyl enol ether of acetophenone with the homologous (dibenzoylacetylene)$Co_2(CO)_6$ complex led to Z-3-[(3,5-diphenyl-2-furyl)methylene]-2–3*H*-benzofuran-1-one, apparently by an aromatic C–H bond activation. The structures of the pyrone and benzofuranone molecules were established either by X-ray crystallography and/or by 2D NMR spectroscopy. A general mechanistic scheme is proposed to account for the versatility of these reactions.

Introduction

At first sight, acetylenedicarbaldehyde, **1**, is an attractive synthon for versatile nucleophilic or pericyclic functionalisation.[1] As shown by Gorgues and coworkers, it can be obtained by formolysis of its diethyl acetal, **2**, but it is unstable, however, in its free state. The inertness of the acetal function under basic conditions precludes the use of **2** as a practical equivalent of **1** for direct nucleophilic functionalisation. Despite the intrinsically poor stability of conventional propargylic cations, the acid-mediated generation of propargylic carbenium centres can be enhanced by complexation of **2** with a $Co_2(CO)_6$ unit.[2] This approach constitutes the first step of the Nicholas reaction of mono-propargylic ethers with neutral nucleophiles,[3] which has been generalised to mono-propargylic acetals.[4] In the latter case, however, 1,1-disubstitution does not occur; instead, acid-catalysed elimination is favoured and leads to α,β-unsaturated-α-ketoalkyne products. To the best of our knowledge, although $Co_2(CO)_6$ complexes of 1,4-bis-propargylic diethers and diesters have been envisioned as precursors for double Nicholas reactions,[5] 1,4-disubstitution of bis-propargylic diacetals has not been reported. Herein, we describe such a reaction of the diacetal complex **3**, and compare it with the parent aldol reaction of (acetylenedicarbaldehyde)$Co_2(CO)_6$, **4**. Indeed, although the preparation of complex **4** was described more than ten years ago by Gorgues' and Le Marouille,[6] its electrophilic reactivity with neutral nucleophiles (condensation with primary amines,[7] Wittig reaction[8]) has hardly been investigated.

As shown in Scheme 1, the diethyl acetal complex **3**, prepared from bis(diethyl acetal) **2** and $Co_2(CO)_8$, was readily converted to the dialdehyde complex **4** according to a de-



Scheme 1. Protected versions of the alkyne and aldehyde functions of acetylenedicarbaldehyde **1**, and the enol ethers **5**−**8** with which they can react.

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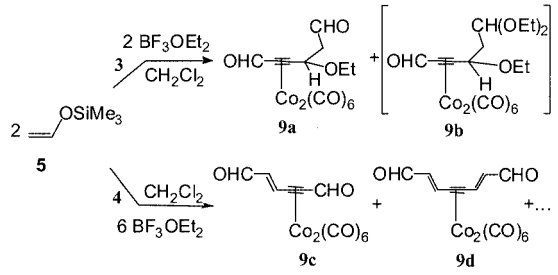
scribed method,[9] and the reactivity of complexes **3** and **4** with the four enol ethers **5**−**8** has been investigated.

Results

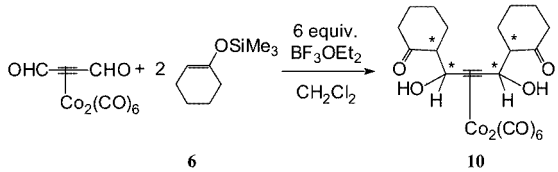
1. Trimethylsilyl Enol Ether of Acetaldehyde (5) and of Cyclohexanone (6)

Treatment of the bis(diethyl acetal) complex **3** with the trimethylsilyl enol ether of acetaldehyde, **5**, in the presence of two equivalents of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 afforded the mono-aldol product **9a** along with ca. 5% of its diethyl acetal form **9b** (the latter could not be isolated in a pure state, but MS and NMR spectral analyses are consistent with the structure). No bis(aldol) derivative was formed (Scheme 2). In a bifunctional version of Hanaoka's reaction of silyl enol ethers with cobalt-complexed propynals,[10] enol ether **5** was also allowed to react with the dialdehyde complex **4** in the presence of six equivalents of $BF_3{\cdot}OEt_2$ in CH_2Cl_2. Dehydrated aldol derivatives such as the symmetrical octyne-diene-dial complex **9d** were obtained, but the selectivity in dialkylation remained poor. Therefore, no systematic study of complex **3** was pursued and attention was focussed on the dialdehyde complex **4**.



Scheme 2. Reactions of diacetal **3** and dialdehyde **4** with **5**, the silyl enol ether of acetaldehyde.

Double aldol addition was exhibited by complex **4** towards the more nucleophilic, and bulkier, trimethylsilyl enol ether of cyclohexanone, **6**. Indeed, as depicted in Scheme 3, the latter reacted with **4** in the presence of six equivalents of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 to afford the bis(aldol) **10** in 53% isolated yield as a statistical mixture of a priori six possible diastereoisomers, four of them being chiral. Despite the high acidity of the medium, no dehydration occured.[11]

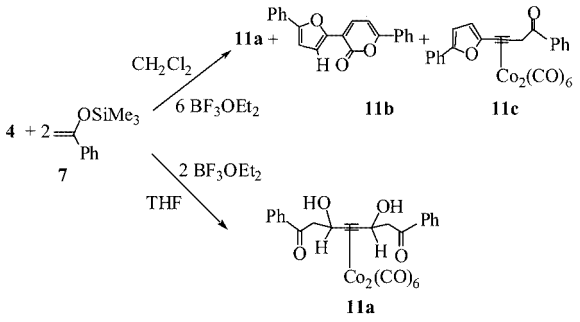


Scheme 3. Double aldol reaction of dialdehyde **4** with **6**, the trimethylsilyl enol ether of cyclohexanone.

2. Trimethylsilyl Enol Ether of Acetophenone 7

The nucleophilicity of acetophenone trimethylsilyl enol ether, **7**, should be intermediate between those of **5** and **6**. Reaction of **7** with dialdehyde complex **4** in the presence of two equivalents of $BF_3{\cdot}OEt_2$ in THF (i.e., in a weakly acidic medium) led to **11a** as a mixture of *meso* and *dl* diastereoisomers.

The chemoselectivity of the reaction depends strongly on the acidity of the medium and, in the presence of six equivalents of $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (use of THF would lower the overall acidity of the medium), the reaction led to three products: as well as the bis(aldol) **11a**, unexpected violet and yellow products were also obtained and were characterised as a phenylfuranobut-3-yn-1-one complex, **11c**,[12] and a furano-2*H*-pyran-2-one, **11b** (Scheme 4). The formation of these compounds is intriguing (see discussion section), but they can clearly be recognized as having been derived from bis(aldol) **11a**.



Scheme 4. Reactions of acetophenone trimethylsilyl enol ether **7**, with the dialdehyde complex **4**, in different solvents.

The mass spectrometric and NMR spectroscopic data for **11b** strongly supported its assignment as a 2-phenylfuran coupled to a phenyl-2*H*-pyran-2-one. Even though the chemical shifts observed in ^{13}C NMR spectrum of **11b** fit almost perfectly with the shifts calculated for the proposed structure, we felt obliged, however, to confirm the regiochemistry unequivocally by means of X-ray crystallography.[13] As shown in Figure 1, **11b** is almost perfectly planar despite the presence of three formally single inter-ring bonds; the torsional dihedral angle between the rings is negligible (3.9°), in marked contrast to the value of ca. 40° in biphenyl.[14] The shortness of the furan−2*H*-pyranone bond (1.43 Å vs. 1.49 Å in biphenyl) and the planarity of the structure suggest some degree of delocalization through this bond; there are, however, no obvious resonance structures, as would have been possible had the lactone functionality been reversed. Moreover, although it is tempting to draw a pyrylium-type structure for the six-membered

ring, it is known that α-pyrones do not exhibit very marked aromatic character.[15]

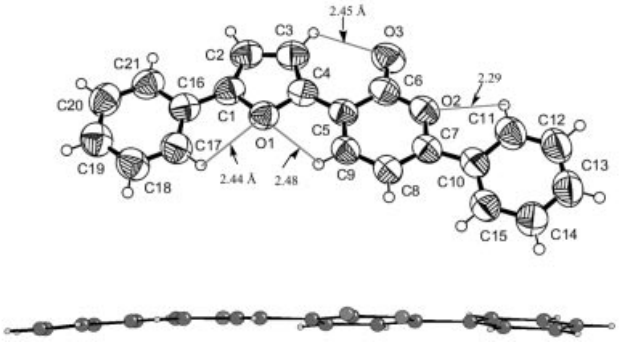


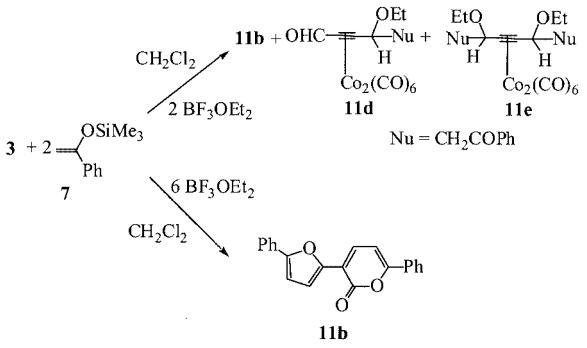
Figure 1. X-ray-crystal structure of pyrone **11b** (Pbca); selected bond lengths (Å): C(1)−C(16) = 1.452(6); C(1)−O(1) = 1.381(4); C(1)−C(2) = 1.355(6); C(2)−C(3) = 1.411(6); C(2)−H(2) = 0.99(5); C(3)−H(3) = 1.01 (5); O(1)−C(4) = 1.384(4); C(4)−C(5) = 1.432(5); C(5)−C(9) = 1.362(5); C(9)−C(8) = 1.408(5); C(8)−C(7) = 1.355(5); C(5)−C(6) = 1.441(5); C(6)−O(3) = 1.211(5); C(6)−O(2) = 1.380(5); C(7)−O(2) = 1.364(4); C(7)−C(10) = 1.454(5); O(2)−C(7)−C(10) = 112.4(3); O(1)−H(9) = 2.48(4); O(1)−H(17) = 2.44(5); O(2)−H(11) = 2.29(4); O(3)−H(3) = 2.45; selected bond angles (degrees): C(1)−O(1)−C(4) = 107.1(3); O(1)−C(1)−C(16) = 116.1(3); C(3)−C(4)−C(5) = 135.1(4); C(4)−C(5)−C(6) = 117.2(3); C(5)−C(6)−O(3) = 127.5(4); C(9)−C(5)−C(4) = 124.4(3); C(7)−O(2)−C(6) = 123.9(3); C(7)−C(8)−C(9) = 119.2(4); C(15)−C(10)−C(7) = 121.0(3); C(11)−C(10)−C(7) = 120.7(4). Selected dihedral angle: O1−C4−C5−C6 = 176.1(3)°.

One might hypothesise that the planar structure is stabilized to some extent by weak H···O interactions between phenyl and furyl C−H bonds with furan and pyranone oxygen atoms.[16] This conformation is found not only in the crystal state, but also in $CDCl_3$ solution, as indicated by ^1H NMR spectroscopic data which reveal no NOE interactions between the "inner" protons of the furan and pyranone rings.

Likewise, reaction of the diacetal complex **3** with **7** afforded *2H*-pyranone **11b** along with a 25:75 mixture of mono- and di-alkylation products, **11d** and **11e**, respectively (Scheme 5). To the best of our knowledge, this example is the first of a double Nicholas reaction with a 1,4-bis-propargylic diacetal. Further treatment with *p*-toluenesulfonic acid converted the reaction mixture to pyranone **11b**, which could also be obtained quantitatively by direct treatment of the diacetal complex **3** with an excess of $BF_3{\cdot}OEt_2$.

To determine the scope of the reaction, another non-enolizable (dicarbonylacetylene)$Co_2(CO)_6$ complex was investigated. Although $Co_2(CO)_6$ complexes of enolisable diketoylacetylenes have been reported to undergo stereoselective catalytic reduction by $Me_2S{\cdot}BH_3$,[17] their electrophilic reactivity has rarely been studied. Therefore, the dibenzoylacetylene complex **12** was prepared and characterised by X-ray crystallography (Figure 2); the metric parameters lie within the normal ranges for alkyne−dicobalt clusters.

Speculation as to the possibility of an interaction between a cobalt centre and a ketonic carbon atom was quelled by the X-ray structure of **12**, which gave no indication of a direct Co···C^+-O^- interaction in the ground



Scheme 5. Reaction of trimethylsilyl enol ether of acetophenone with the diacetal complex **3**.

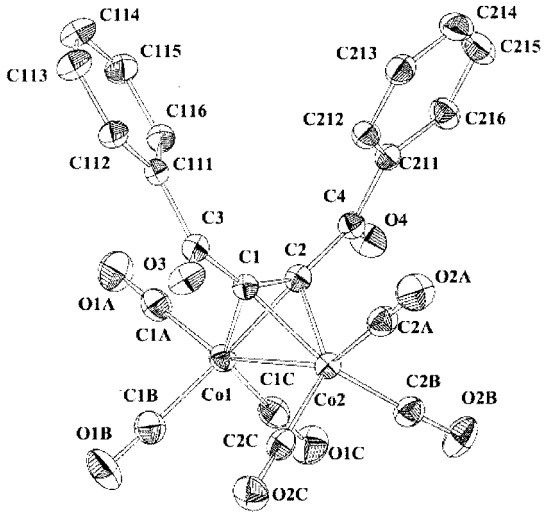
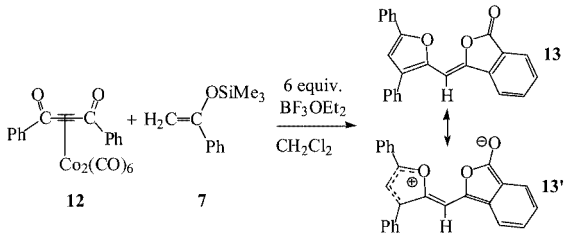


Figure 2. X-ray-crystal structure of complex **12** (*P*21/*c*); selected bond lengths (Å): Co(1)−C(1) = 1.960(4); Co(1)−C(2) = 1.934(4); Co(1)−Co(2) = 2.4618(8); Co(2)−C(2) = 1.973(4); Co(2)−C(1) = 1.954(4); O(3)−C(3) = 1.226(5); O(4)−C(4) = 1.219(5); C(1)−C(2) = 1.360(5); C(1)−C(3) = 1.466(5); C(2)−C(4) = 1.465(5); selected bond angles (degrees): C(2)−C(1)−C(3) = 147.0(4); C(1)−C(2)−C(4) = 147.4(4); O(4)−C(4)−C(2) = 119.4(3); O(3)−C(3)−C(1) = 119.3(3).

state. The carbonyl function of **12** could, however, be activated by a Lewis acid. Nevertheless, as expected from electronic and steric considerations, the reaction of **12** with the silyl enol ether of acetophenone, **7**, in the presence of $BF_3{\cdot}OEt_2$ proceeded much more slowly than the corresponding reaction of the acetylenedicarbaldehyde complex **4**. Despite low conversion (32%), furano-lactone **13** was the sole isolated product (Scheme 6). To the best of our knowledge, this is the first preparation of a furyl-substituted methyleneisobenzofuranone, although analogous aryl and 2-thienyl derivatives are known.[18] While the latter systems are conventionally prepared by classical Gabriel condensation−decarboxylation of acetic acid derivatives with phthalic anhydride, we suggest that the furyl product **13** apparently results from an unprecented sequence of reactions: monoaldol reaction, cyclisation, aromatic C−H acti-

vation, cyclocarbonylation and decomplexation. These mechanisms are further discussed below.

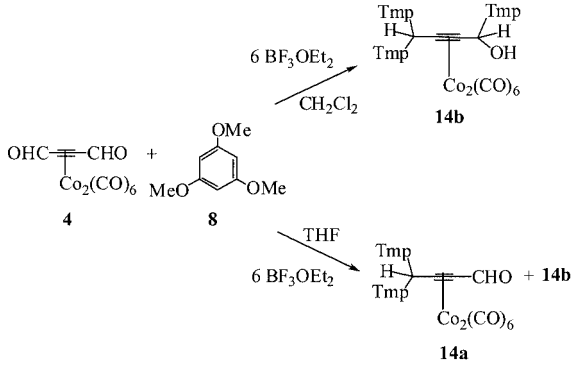


Scheme 6. One-step synthesis of a furyl-substituted methyleneisobenzofuranone **13**.

Further insight into the structure of **13** was gained by the detection of NOE enhancements between the central vinylic proton and the neighbouring aromatic protons (see Exp. Sect.). These observations indicate a near-planar structure, with *Z* stereochemistry about the central enol double bond, and a transoid conformation of the dioxybutadiene sequence, PhC=C(−O)−CH=C(−O). The planarity of the molecule, reminiscent of that of the furano-pyranone **11b**, is here explained by the highly stabilized isobenzofuran resonance form, **13′**, in which the furan oxygen atom donates an electron pair and the carbonyl oxygen atom acquires a negative charge. The positive charge on the furan oxygen atom can also be alleviated by electron delocalisation from the two appropriately positioned phenyl substituents. The syn arrangement of the furan and benzofuranone ring oxygen atoms might also be assisted by the electrostatic interaction between them in the dipolar resonance form.

3. 1,3,5-Trimethoxybenzene 8

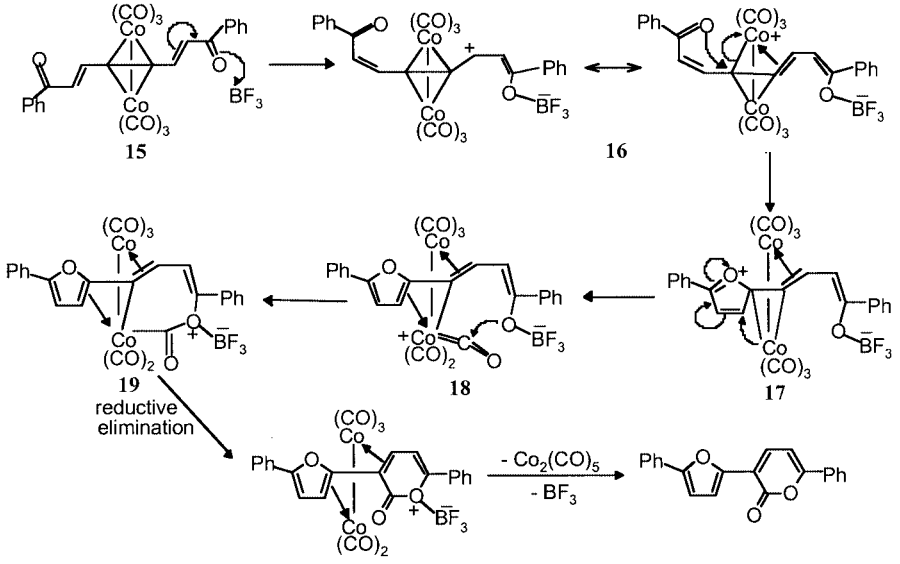
In CH_2Cl_2, reaction of **4** with four equivalents of 1,3,5-trimethoxybenzene **8**[19] led to the tris-arylation product **14b** in 50% yield (Scheme 7). This solvent is, however, not inert: A chlorinated product **14c** was also produced, for which mass spectrometric data suggest the formula $[(CCl)_2\{C_6H_2(CH_3O)_3\}_2(HCOCCCHO)Co_2(CO)_6]$.[20] In THF and in the presence of six equivalents of $BF_3{\cdot}OEt_2$, eight equivalents of **8** were necessary to obtain **14a** in 35% yield and **14b** in 52% yield. Despite the use of a large excess of nucleophile, the 1,1,4,4-tetraarylbut-2-yne complex could not be detected.



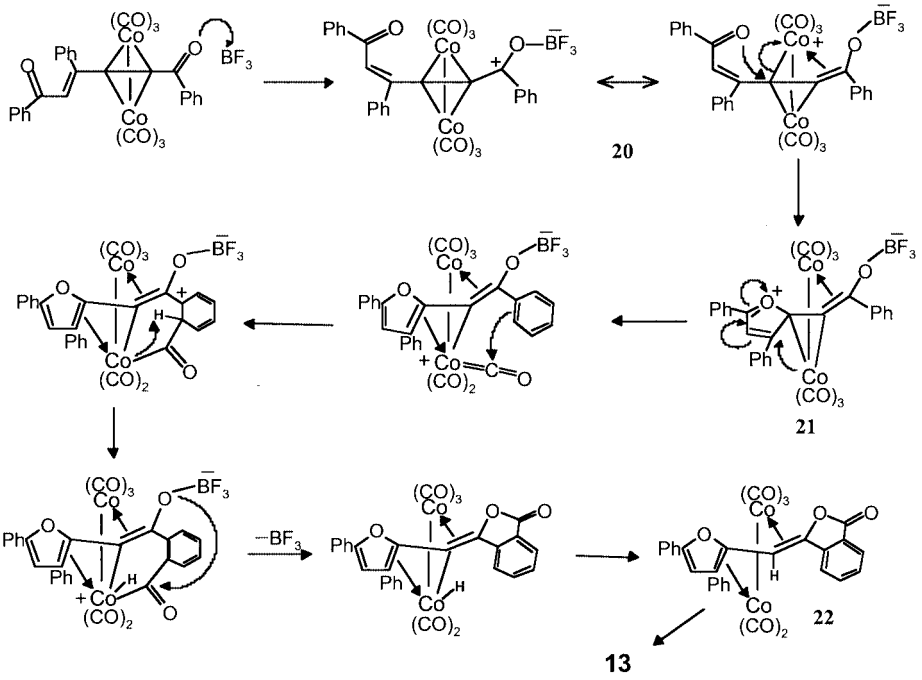
Scheme 7. Reaction of 1,3,5-trimethoxybenzene with dialdehyde complex **4**; Tmp = 2,4,6-trimethoxyphenyl.

Discussion

The novel products, **11b** and **13**, arising from the reactions of complexes **3** (or **4**) and **12**, respectively, with the enol ether of acetophenone, **7**, merit particular comment in contrast to the behaviour of the other enol ethers in dichloromethane. One can write a mechanism (Scheme 8) in which pyrone **11b** results from a series of tandem or sequential elementary steps, namely two aldol reactions, cyclisation, cyclocarbonylation, reductive elimination, and finally decomplexation.[21] Reaction of the bis(enone) complex, **15**, with BF_3 would generate a carbocation, **16**, in which the charge is delocalised by interaction of the vacant p orbital



Scheme 8. Proposed mechanism for the formation of **11b** from **4** and **7**.



Scheme 9. Proposed mechanism for the formation of **13** from **12** and **7**.

on the α-carbon atom with a filled d orbital on cobalt. This intermediate now can induce attack on an alkyne cluster carbon atom to generate a particularly favourable carbocation, **17**, that is stabilized not only by the adjacent phenyl and allyl moieties, but also by the oxygen atom of the newly formed furan ring. The net result of this rearrangement is to bring about a one-bond α-slippage of the μ-$Co_2(CO)_6$ unit, as in **18**. The system is now poised for a nucleophilic attack by the oxygen atom on a relatively electron-poor cobalt carbonyl ligand to produce the seven-membered metallacycle **19**. Reductive elimination to form the pyrone ring and subsequent decomplexation yields **11b**. We hypothesize that the specificity arises because the analogous cations derived from the enol ethers of other ketones and aldehydes, such as **5** and **6**, would not be as stable as **17**.

In a similar fashion, the reaction of **7**, the enol ether of acetophenone, with the dibenzoylacetylene complex **12** in the presence of BF_3 can proceed by initial generation of the cobalt-stabilized cation, **20**, rearrangement to form **21**, the multiply stabilized analogue of **17**, and subsequent attack by a phenyl ring on the carbonyl ligand bonded to a positively charged cobalt centre; in fact, this latter step is essentially a Friedel−Crafts acylation. Finally, hydrogen transfer (probably via the cobalt centre) and cyclization to yield the benzofuranone complex, **22**, leads ultimately to the observed product **13**. We note that, in the acidic medium, the *Z* enone double bond required for the initial cyclization leading to **21** can be generated in equilibrium with the nonproductive *E* configuration.

Conclusions

Acetylenedicarbaldehyde is shown to be a useful and versatile reagent for C−C bond-forming reactions. This exploratory work reveals the novel scope for propargylic functionalisation on the basis of the Nicholas methodology, including (i) the possibility of an addition process at a bis-propargylic dialdehyde instead of the classical substitutions at ether and acetal functions; (ii) the possibility of 1,1-bis- vs. 1,1,4-tris-*aryl*ation of a bis-propargylic dialdehyde; (iii) the possibility of one-pot multistep reactions (aldol, dehydration, cyclization, cyclocarbonylation) of the trimethylsilyl enol ether of acetophenone for the synthesis of novel 2*H*-pyran-2-one derivatives. The generality and the selectivity of the reactions clearly merit further investigations (e.g., with respect to the nature of the auxiliary Lewis acid) and, in a complementary study, the reactivity of the acetylenedicarbaldehyde complex **4** with anionic C-nucleophiles is the topic of the preceding report.[22]

Experimental Section

THF and diethyl ether were distilled over Na/benzophenone. Pentane and dichloromethane were distilled over P_2O_5. Commercial silyl enol ethers **5**−**7** and trimethoxybenzene **8** were used as received. Dibenzoylacetylene,[23] 1,1,4,4-tetraethoxybut-2-yne **2**,[24] and complexes **3** and **4**,[22] were prepared according to published procedures. Elemental analyses were performed at the Service de Microanalyse du L.C.C. on a Perkin−Elmer 2400 apparatus. IR spectra were recorded on a Perkin−Elmer Spectrum GX FT-IR

spectrometer using a CaF_2 cell. NMR spectra were recorded on AC 200, AM 250 or AMX 400 Bruker spectrometers. Positive chemical shifts to high frequency are expressed in ppm relative to an internal tetramethylsilane reference.

X-ray Crystallographic Structure Determinations of 11b and 12: Data were collected at low temperature (T = 270 K for **11b**, T = 180 K for **12**) on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device, and using graphite-monochromated Mo-K radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by means of a least-squares refinement of a set of well-measured reflections, and crystal decay was monitored during data collection; no significant fluctuations in intensity were observed. The structures were solved by Direct Methods using the program SIR92,[25] and refined by least-squares procedures on F^2 with SHELXL-97.[26] All hydrogen atoms were located on difference Fourier maps, but introduced and refined by using a riding model, except for hydrogen atoms H(2) and H(3) in **11b**, which were isotropically refined. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement the following weighting scheme was used: $w = 1/[2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Molecules were drawn by using the program ORTEP32,[27] with 50% probability displacement ellipsoids for non-hydrogen atoms.

Dibenzoylacetylene Complex 12: Dibenzoylacetylene (0.810 g, 3.46 mmol) and $Co_2(CO)_8$ (1.18 g, 3.46 mmol) were dissolved in diethyl ether (60 mL). A brown-red precipitate readily deposited. The solution was filtered through celite, and then evaporated to dryness. The brown residue (1.596 g) was recrystallised from cold diethyl ether/pentane. After evaporation and drying under vacuum, complex **12** was obtained as a violet-black microcrystalline solid (1.53 g, 85%). M.p. 162 °C. MS (FAB/DMF): m/z = 561, 521 ($[MH]^+$), 493 ($[MH - CO]^+$), 464 ($[M - 2CO]^+$), 437 ($[MH - 3CO]^+$), 408 ($[M - 4CO]^+$), 380 ($[M - 5CO]^+$). IR ($CDCl_3$) ν_{CO} = 2107 (s), 2073 (vs) 2050 (s) cm^{-1}; $\nu_{PhC=O}$ = 1644 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.35 (m, 4 H, *m*-C*H*), 7.48 (m, 2 H, *p*-C*H*), 7.85 (m, 4 H, *o*-C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 63 MHz): δ = 85.40 (*C*≡*C*), 128.5 and 128.7 (*o*- and *m*-*C*H), 133.6 (*p*-*C*H), 135.7 (*ipso*-*C*CO), 192.0 (Ph*C*=O), 197.2 (br, $Co_2(CO)_6$] ppm. X-ray diffraction analysis was performed on a single crystal of the complex.

Reaction of Silylenol Ether 5 with Dialdehyde Complex 4: Acetylenedicarbaldehyde complex **4** (0.310 g, 0.84 mmol) and trimethylsilyl enol ether **5** (0.251 mL,1.68 mmol) were dissolved in CH_2Cl_2 (15 mL) at −78 °C. Six equivalents of $BF_3{\cdot}OEt_2$ (0.640 mL, 5.05 mmol) were added, and the mixture was stirred for 2 h between −78 °C and 25 °C. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution. The organic phase was separated, washed with brine and water, dried over $MgSO_4$, filtered and then evaporated to dryness. The residue was chromatographed over silica gel eluting with heptane/EtOAc mixtures of increasing polarity, starting with a ratio of 90:10. Upon elution with heptane/EtOAc (70:30) and subsequent evaporation, first the dialdehyde complex **4** was recovered (0.010 g, 3%), followed by eliminated monoaldol product **9c** as an orange oil (0.065 g, 20%). IR ($CDCl_3$): $\nu_{CoC\equiv O}$ = 2107 (s), 2074 (vs), 2047 (s) cm^{-1}; $\nu_{HC=O}$ = 1682 (s), 1603 (s) cm^{-1}. MS (DCI/NH_3): m/z = 412 ($[M + NH_4]^+$), 395 ($[MH]^+$), 367 ($[MH - CO]^+$). ^1H NMR ($CDCl_3$): δ = 6.54 (dd, $^3J_{H,H}$ = 15.0, $^3J_{H,H}$ = 7.6 Hz, 1 H, =C*H*−CHO), 7.75 (d, $^3J_{H,H}$ = 15.0 Hz, 1 H, ≡C−C*H*=C), 9.74 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, =CH−C*H*O), 10.36 (s, 1 H, ≡C−C*H*O) ppm. ^{13}C NMR ($CDCl_3$): δ = 86.2 (≡*C*−CHO), 90.5 (CCH−C≡), 134.6 (=*C*H−CHO), 149.9 (H*C*=CCHO), 196.7 [br, $Co_2(CO)_6$] ppm. Quaternary (η²-*C*≡*C*)Co carbon atoms were not detected. Elution with 60:40 heptane/EtOAc and evaporation afforded di-eliminated dialdol product **9d** as a brown oil (0.017 g, 5%). IR ($CDCl_3$): $\nu_{CoC\equiv O}$ = 2103 (s), 2070 (vs), 2044 (s) cm^{-1}; $\nu_{HC=O}$ = 1680 (s) cm^{-1}. MS (DCI/NH_3): m/z = 438 ($[M + NH_4]^+$), 421 ($[MH]^+$), 391 ($[MH - CO]^+$). ^1H NMR ($CDCl_3$): δ = 6.50 (dd, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 7.5 Hz, 2 H, =C*H*−*C*HO), 7.80 (d, $^3J_{H,H}$ = 12.0 Hz, 2 H, ≡C−C*H*=C), 9.75 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, =CH−C*H*O) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 83.50 (*C*≡*C*), 134.10 (=*C*H−CHO), 150.85 (H*C*=CCHO), 197.67 [br, $Co_2(CO)_6$] ppm.

Elution with heptane/EtOAc (40:60) and evaporation afforded a brown oil (0.052 g) consisting of an unidentified mixture of aldehyde products.

Reaction of Silylenol Ether 5 with Bis(diethyl acetal) Complex 3: Acetylenedicarbaldehyde bis(diethyl acetal) complex **3** (0.070 g, 0.135 mmol) and two equivalents of silyl enol ether **5** (0.041 mL, 0.032 g, 0.27 mmol) were dissolved in CH_2Cl_2 (3 mL) at −78 °C. Two equivalents of $BF_3{\cdot}OEt_2$ (0.034 mL, 0.27 mmol) were added, and the mixture was warmed to 10 °C over a 30 min period. The medium was quenched with saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2. The organic phase was separated, dried over $MgSO_4$, and then evaporated to dryness. The crude product was chromatographed over silica gel eluting with pentane/Et_2O mixtures of increasing polarity.

Elution with pentane/Et_2O (60:40) and evaporation afforded at first traces of impure monodiethyl acetal **9b** as an orange oil (0.003 g, ≈ 4%). MS (DCI/NH_3): m/z = 432 ($[M + NH_4]^+$), 515 ($[MH]^+$). ^1H NMR ($CDCl_3$): δ = 1.20 (t, 9 H, C*H*$_3$), 2.06 [t, 2 H, C*H*$_2$CH(OEt)$_2$], 3.52−3.76 (3 m, 6 H, OC*H*$_2$Me), 4.55 (t, 1 H, C*H*OEt), 4.78 [t, 1 H, C*H*(OEt)$_2$], 10.30 (s, 1 H, ≡C−C*H*O) ppm. Elution with pentane/Et_2O (50:50) and evaporation afforded dialdehyde complex **9a** as an orange oil (0.027 g, 46%). IR ($CDCl_3$): $\nu_{CoC\equiv O}$ = 2105 (s), 2070 (vs), 2046 (s) cm^{-1}; $\nu_{HC=O}$ = 1725 (s), 1666 (s) cm^{-1}. MS (DCI/NH_3): m/z = 458 ($[M + NH_4]^+$), 441 ($[MH]^+$), 395 ($[MH - EtO]^+$). ^1H NMR ($CDCl_3$): δ = 1.20 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, C*H*$_3$); 2.83 and 3.02 (2 dd, $^3J_{H,H}$ = 4.5 Hz and $^3J_{H,H}$ = 7.8, $^2J_{H,H}$ = 17.3 Hz, 2 H, C*H*$_2$CHO), 3.70 (2 q, 2 H, OC*H*$_2$Me), 5.00 (dd, $^3J_{H,H}$ = 4.3, $^3J_{H,H}$ = 7.8 Hz, 1 H, C*H*OEt), 9.85 (br s, $^3J_{H,H}$ < 1 Hz, 1 H, CH$_2$-C*H*O), 10.27 (s, 1 H, ≡C−C*H*O) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.0 (*C*H$_3$), 51.1 (O*C*H$_2$Me), 66.4 (*C*H$_2$CHO), 190.5 (CH$_2$*C*HO), 197.8 [br, $Co_2(CO)_6$], 199.1 (≡C−CHO) ppm.

Dialdol 11: Dialdehyde complex **4** (0.300 g, 0.82 mmol) and two equivalents of acetophenone silyl enol ether **7** (0.334 mL, 1.6 mmol) were dissolved in THF (20 mL) at −78 °C. Two equivalents of $BF_3{\cdot}OEt_2$ (0.206 mL, 1.6 mmol) were added, the solution became lighter in colour, and then the mixture was warmed to room temperature overnight. The resulting red solution was evaporated to dryness, and the residue was dissolved in Et_2O. The ethereal phase was washed with a saturated aqueous $NaHCO_3$ solution and with water, dried over $MgSO_4$, and then the solvents evaporated to dryness. The crude material was chromatographed over silica gel eluting with pentane/Et_2O (80:20). Dialdol **11a** was obtained in two fractions (0.136 g of the less-polar diastereoisomer **11a1**, then 0.131 g of the more-polar diastereomer **11a2**) as an orange oil (0.267 g in total, 0.44 mmol, 54%).

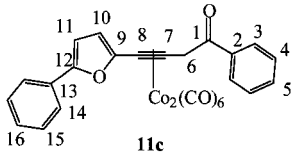
IR ($CDCl_3$): ν_{O-H} = 3541 (m) cm^{-1}; ν_{sp2C-H} = 3069 (w) cm^{-1}; ν_{sp3C-H} = 2909 (w) cm^{-1}; $\nu_{CoC\equiv O}$ = 2096 (s), 2057 (vs), 2037 (s) cm^{-1}; $\nu_{PhC=O}$ = 1677 (s) cm^{-1}; $\nu_{C=C}$ = 1598 (m), 1581 (m) cm^{-1}; another band at 1450 (m) cm^{-1}. MS (DCI/NH_3): m/z = 458 ($[M + NH_4]^+$), 441 ($[MH]^+$), 395 ($[MH - EtO]^+$).

Diastereoisomer 11a1: (0.136 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.39 (dd, $^2J_{H,H}$ = 17.6, $^3J_{H,H}$ = 8.8 Hz, 2 H, C*H*), 3.65 (dd, $^2J_{H,H}$ = 17.6, $^3J_{H,H}$ = 2.0 Hz, 2 H, C*H*), 4.20 (d, $^3J_{H,H}$ = 2.2 Hz, 2 H, exchangeable with D_2O, O*H*), 5.52 (m, 2 H, C*H*O), 7.48 (pseudo-triplet, 4 H, *m*-C*H*), 7.61 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-C*H*), 7.98 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 47.1 (t, $^1J_{C,H}$ = 127.0 Hz, *C*H$_2$), 68.8 (d, $^1J_{C,H}$ = 147.6 Hz, *C*HOH), 98.7 (s, *C*≡*C*), 128.2 and 128.8 (2 d, $^1J_{C,H}$ = 161.0 Hz, *o*-*C*H and *m*-*C*H), 133.8 (d, $^1J_{C,H}$ = 161.0 Hz, *p*-C*H*), 136.4 (s, *ipso*-*C*), 199.3 (2 s, Ph*C*=O, $Co_2(CO)_6$].

Diastereoisomer 11a2: (0.1321 g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.39 (m, 2 H, C*H*), 3.58 (dd, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 3.3 Hz, 2 H, C*H*), 4.36 (d, $^3J_{H,H}$ = 2.6 Hz, 2 H, exchangeable with D_2O, O*H*), 5.54 (m, 2 H, C*H*O), 7.49 (pseudo-triplet, 4 H, *m*-C*H*), 7.61 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-C*H*), 7.97 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 46.8 (t, $^1J_{C,H}$ = 127.0 Hz, *C*H$_2$), 68.5 (d, $^1J_{C,H}$ = 147.6 Hz, *C*HOH), 99.2 (s, *C*≡*C*), 128.2 and 128.8 (2 d, $^1J_{C,H}$ = 161.0 Hz, *o*-*C*H and *m*-*C*H), 133.8 (d, $^1J_{C,H}$ = 161.0 Hz, *p*-C*H*), 136.4 (s, *ipso*-*C*), 199.1 and 199.3 (2 s, Ph*C*=O, $Co_2(CO)_6$] ppm.

Furans 11b and 11c: Dialdehyde complex **4** (0.200 g, 0.54 mmol) and two equivalents of acetophenone silyl enol ether **7** (0.223 mL, 1.09 mmol) were dissolved in CH_2Cl_2 (10 mL) at −78 °C. Six equivalents of $BF_3{\cdot}OEt_2$ (0.413 mL, 3.26 mmol) were added and the mixture was warmed to room temperature over 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic phase was then separated, washed with water and brine, dried over $MgSO_4$, filtered and then the solvents evaporated to dryness. The residue was chromatographed over silica gel eluting with hexane/CH_2Cl_2 mixtures of increasing polarity.

Elution with hexane/CH_2Cl_2 (65:35) and evaporation afforded **11c** as a violet solid (0.005 g, 16%). IR ($CDCl_3$): ν_{sp2C-H} = 2978 (w), 2927 (w), 2875 (w) cm^{-1}; $\nu_{CoC\equiv O}$ = 2093 (s), 2058 (vs), 2031 (s) cm^{-1}; $\nu_{PhC=O}$ = 1601 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 590 ([M + NH_4]$^+$), 545 ([MH − CO]$^+$), 517 ([MH − 2CO]$^+$). ^1J and long-range ^{1}H-^{13}C HMQC 2D spectra led to the following assignments for the ^{1}H and ^{13}C signals.



11c

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.70 (s, 2 H, H-6), 6.75 (second-order triplet-like, $^3J_{H,H}$ = 3.6 Hz, 2 H, H-10, H-11), 7.31 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, H-16), 7.42 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H-4 or H-15), 7.55 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H15 or H-4), 7.67 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, H-5), 7.71 (dd, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 0.8 Hz, 2 H, H-14), 8.11 (br d, $^3J_{H,H}$ = 8 Hz, 2 H, H-3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 42.86 (C-6), 77.45 (C-8), 88.55 (C-7), 107.84 (C-12), 112.94 (C-9), 124.16 (C-14), 128.12 (C-16), 129.04 (C-3), 129.27 and 129.31 (C-4 and C-15), 130.90 (C-5), 134.17 (C-13), 136.51 (C-2), 150.51 (C-9), 155.37 (C-12), 195.55 (C-1), 199.35 [$Co_2(CO)_6$] ppm.

Elution with hexane/CH_2Cl_2 (40:60) and evaporation afforded **11b** as yellow plates (0.024 g, 14%). UV ($CDCl_3$): λ_{max} = 422, λ_{max-1} = 306 nm. IR ($CDCl_3$): ν_{sp2C-H} = 2924 (w), 2853 (w) cm^{-1}; $\nu_{pyroneC=O}$ = 1722 (s) cm^{-1}; other bands at 1624 (s),1519 (m), 1496 (m), 1484 (m), 1449 (m), 1392 (w), 1024 (s) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 315 ([MH]$^+$). ^1J and long-range ^{1}H-^{13}C HMQC 2D spectra led to the following assignments for the ^{1}H and ^{13}C signals (atom numbering from Figure 1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.81 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, H-2), 6.87 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, H-8), 7.32 (t, $^3J_{H,H}$ ≈ 7 Hz, 1 H, H-19), 7.41 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, H-3), 7.44 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H-18), 7.48 (second-order t-like, $J_{H,H}$ = 6.6 Hz, 1 H, H-13), 7.48 (second-order d-like, $J_{H,H}$ = 6.4 Hz, 2 H, H-12), 7.76 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H-17), 7.89 (m, 2 H, H-11), 7.95 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, H-9). The assignment of the *o*-C*H* protons of the two phenyl rings with respect to the outer =C*H* protons of the furan−pyrone system was confirmed by 1D ^{1}H NOE dpfgse (Double-Pulse Field Gradient Selective Experiment) (T_m = 800 ms). Zero NOE enhancement was recorded between the inner =C*H* protons of the furan−pyrone system, showing that they lie *anti* to each other with respect to the furan−pyrone bond. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 102.25 (C-8), 108.47 (C-2),114.73 (C-3), 116.50 (C-5), 124.41 (C-17), 125.78 (C-11), 128.30 (C-19), 129.20 (C-18), 129.40 (C-12), 130.50 (C-16), 131.00 (C-13), 131.64 (C-10), 134.37 (C-9), 147.90 (C-4), 154.81 (C-1), 158.54 (C-7) ppm. X-ray diffraction analysis was performed on a single crystal of the complex.

Dialdol 10: Dialdehyde complex **4** (0.300 g, 0.82 mmol) and two equivalents of cyclohexanone silyl enol ether **6** (0.317 mL, 1.60 mmol) were dissolved in CH_2Cl_2 (20 mL) at −78 °C. Six equivalents of $BF_3{\cdot}OEt_2$ (0.620 mL, 4.9 mmol) were added, and the mixture was warmed to room temperature over 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The organic phase was then separated, washed with water, dried over $MgSO_4$, and then the solvents were evaporated. A single spot appeared on silica gel TLC (R_f = 0.40; pentane/EtOAc, 80:20). The residue was chromatographed over silica gel eluting with a hexane/EtOAc mixture (90:10). Dialdol **10** was obtained as a brown oil (0.244 g, 0.43 mmol, 53%) consisting of a mixture of the six possible diastereoisomers (four of them being chiral).

IR ($CDCl_3$): ν_{O-H} = 3447 (m) cm^{-1}; ν_{sp2C-H} = 2945 (w) cm^{-1}; ν_{sp3C-H} = 2867 (w) cm^{-1}; $\nu_{CoC\equiv O}$ = 2094 (s), 2058 (vs), 2031 (s) cm^{-1}; $\nu_{C=O}$ = 1698 (s) cm^{-1}; $\nu_{C=C}$ = 1598 (m), 1581 (m) cm^{-1}; other bands at 1450 (m), 1431 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 582 ([M + NH_4]$^+$), 547 ([MH − H_2O]$^+$). ^{1}H NMR [(CD_3)$_2$CO/D_2O, 250 MHz]: δ = 1.72−1.92 [12 H, CCH(C*H*$_2$)$_3$], 2.37−2.46 (4 H, C*H*$_2$C=O), 2.75 (br, 2 H, C−C*H*−C=O), 4.70−5.54 (br, 4 H, C*H*O*H*) ppm. ^{13}C NMR [(CD_3)$_2$CO/D_2O, 50 MHz]: δ = 23.7−32.6 [(*C*H$_2$)$_3$], 40.5−43.1 (*C*H$_2$CO), 58.6−59.5 (OC*C*H-CHOH), 68.8−73.0 (*C*HOH), 200.7 [br, $Co_2(CO)_6$], 210.5−214.3 (*C*=O) ppm.

Reaction of Silylenol Ether 7 with Bis(diethyl acetal) Complex 3: Acetylenedicarbaldehyde bis(diethyl acetal) complex **3** (0.100 g, 0.194 mmol) and two equivalents of silylenol ether **7** (0.080 mL, 0.075 g, 0.39 mmol) were dissolved in CH_2Cl_2 (4 mL) at −78 °C. Two equivalents of $BF_3{\cdot}OEt_2$ (0.050 mL, 0.39 mmol) were added and the reaction medium was stirred overnight between −78 °C and room temperature. The mixture was quenched with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The organic phase was separated, washed with brine, dried over $MgSO_4$, and then evaporated to dryness. The crude product was chromatographed over silica gel eluting with pentane/EtOAc mixtures of increasing polarity starting from 90:10; two fractions were recovered. After evaporation of the solvents, the less-polar fraction gave a mixture of mono-aldol **11d** (25%) and bis(aldol) **11e** (75%) as an orange oil (0.017 g). After evaporation of the solvents, the more polar fraction gave pure furano-pyrone **11b** as a yellow solid (0.011 g, 18%).

Mono-aldol 11d: MS (DCI+/NH_3): *m*/*z* = 517 ([MH]$^+$), 489 ([MH − CO]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.16 (t, $^3J_{H,H}$ =

6.9 Hz, CH_3), 3.30 and 3.7 (hidden) (2 m, diastereoisotopic CH_2COPh), 3.71 (br q, $^3J_{H,H} \approx 7$ Hz, CH_2O), 5.19 (pseudo-triplet, $^3J_{H,H} \approx 6$ Hz, 1 H, C*H*OEt), 7.43−7.59 (m, *m*- and *p*-C*H*), 7.92−8.08 (m, *o*-C*H*), 10.26 (s, 1 H, C*H*O) ppm.

Bis(aldol) 11e: MS (DCI+/NH_3): *m*/*z* = 636 ([MH]$^+$), 489 ([M + NH_4 − EtOH]$^+$), 619 ([MH − EtOH]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.15 (t, $^3J_{H,H}$ = 6.9 Hz, CH_3), 3.22 (dd, $^2J_{H,H}$ = 16.8, $^3J_{H,H}$ = 4.5 Hz), 3.66 (dm, $^2J_{H,H}$ = 7.5 Hz), 3.71 (br q, $^3J_{H,H} \approx 7$ Hz, CH_2O), 5.26 (dd, *J* = 4.5, *J* = 7.5 Hz, C*H*OEt), 7.43−7.59 (m, *m*- and *p*-C*H*), 7.92−8.08 (m, *o*-C*H*) ppm.

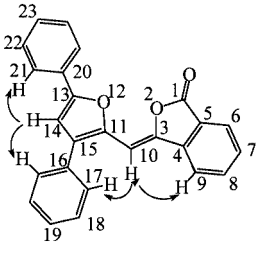
Furanoisobenzofuranone 13: Dibenzoylacetylene complex **12** (0.317 g, 0.61 mmol) and two equivalents of trimethylsilyl enol ether **7** (0.25 mL, 1.22 mmol) were dissolved in CH_2Cl_2 (20 mL) at −60 °C. Six equivalents of $BF_3{\cdot}OEt_2$ (0.464 mL, 3.66 mmol) were added, and the mixture was stirred for 1 h between −78 °C and 25 °C, then for 2.5 h at 50 °C. After stirring for another 24 h at room temperature, no further progress of the reaction was detected by TLC. The reaction was then quenched by addition of saturated aqueous $NaHCO_3$ solution (20 mL). The organic phase was separated, washed with water, dried over $MgSO_4$, filtered and then evaporated to dryness. The residue was chromatographed over silica gel eluting with heptane/EtOAc mixtures of increasing polarity, starting with a ratio of 90:10.

Elution with heptane/EtOAc (80:20) and evaporation afforded starting material **12** (0.215 g, 68% recovery).

Elution with heptane/EtOAc (70:30) and evaporation afforded **13** as a brown microcrystalline yellow solid (0.02 g, 9%). IR ($CDCl_3$): $\nu_{C=O}$ = 1781(sh), 1770 (s) cm^{-1}; $\nu_{C=C-O}$ = 1653 (w) cm^{-1}; $\nu_{aromaticC=C}$ = 1603 (m), 1450 (m) cm^{-1}; ν_{C-O} = 1083 (m) cm^{-1}; bands of alcohol impurities were also detected at 3691 (m), 3364 (br m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 382 ([M + NH_4]$^+$), 365 ([MH]$^+$).

^1J and long-range ^{1}H-^{13}C HMQC 2D spectra led to the following assignments for the ^{1}H and ^{13}C signals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ : 6.53 (s, H-10), 6.95 (s, H-14), 7.36 (tt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, H-23), 7.44 (tt, $^3J_{H,H}$ = 6.8, $^4J_{H,H}$ = 1.6 Hz, H-19), 7.50 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H-22), 7.55 (two second-order m, 4 H, H-17, H-18), 7.55 (t, ^3J = 7.8 Hz, H-7), 7.69 (second-order m, H-8), 7.71 (second-order m, H-9), 7.93 (dm, $^3J_{H,H}$ = 7.7 Hz, 2 H, H-21), 7.98 (dt, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.6 Hz, H-6) ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ = 94.8 (C-10), 108.3 (C-14), 120.2 (C-8), 123.9 (C-5), 124.8 (C-21), 126.1 (C-6), 128.2 (C-19), 128.7 (C-23), 128.9 (C-17), 129.3 (C-18), 129.4 (C-22), 129.9 (C-7), 130.6 (C-20), 133.6 (C-16), 134.6 (C-9), 140.5 (C-4), 143.4(C-3), 144.9 (C-11), 155.9 (C-13), 167.6 (C-1) ppm.

The assignment of the *Z* stereochemistry of enol carboxylate double bond and of the transoid conformation of the PhC=C(−O)−CH=C(−O) butadiene unit was determined by 1D dpfgs ^{1}H NOE experiments (Tm = 600 ms): NOE enhancement was observed from H-10 to H-9 and H-17, and from H-14 to H-17 and H-21.



13

Reaction of 4 with Trimethoxybenzene 8 in THF. Synthesis of 14a and 14b: Acetylenedicarbaldehyde complex **4** (0.200 g, 0.54 mmol) and eight equivalents of trimethoxybenzene **8** (0.732 g, 4.34 mmol) were dissolved in THF (10 mL) at −78 °C. Six equivalents of $BF_3{\cdot}OEt_2$ (0.413 mL, 3.26 mmol) were added and the mixture was warmed to room temperature over 1 h; the reaction was completed by stirring overnight at room temperature. The solvent was removed under reduced pressure, and the residue was treated with dichloromethane and saturated aqueous $NaHCO_3$. The organic phase was then separated, washed with brine, dried over $MgSO_4$, and the solvents evaporated. The residue was chromatographed over silica gel eluting with pentane/EtOAc mixtures of increasing polarity, starting with a ratio of 80:20.

Elution with pentane/EtOAc (80:20) and evaporation afforded the excess trimethoxybenzene **8.**

Elution with pentane/EtOAc (70:30) and evaporation afforded the diarylbutynaldehyde **14a** (0.129 g, 35%).

IR ($CDCl_3$): $\nu_{CoC\equiv O}$ = 2094 (s), 2058 (vs), 2031 (vs) cm^{-1}; $\nu_{HC=O}$ = 1663 (s) cm^{-1}; $\nu_{aromaticC=C}$ = 1602 (s), 1467 (m) cm^{-1}; other bands at 2939 (w, sharp), 1229 (m), 1205 (m), 1152 (m), 1131 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 687 ([MH]$^+$), 659 ([MH − CO]$^+$), 519. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 3.70 (s, 12 H, *o*-C−OCH_3), 3.75 (s, 6 H, *p*-C−OCH_3), 6.04 (s, 4 H, *m*-C*H*), 6.59 (s, 1 H, Ar_2CH), 10.25 (s, 1 H, C*H*O) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 36.5 (Ar_2CH), 55.1 (*o*-C−OCH_3), 55.3 (*p*-C-OCH_3), 89.2 (≡*C*−CHO), 90.4 (*m*-*C*H), 105.0 (≡*C*−CHAr$_2$), 112.6 (*ipso*-*C*), 158.9 (*o*-*C*OMe), 159.8 (*p*-*C*OMe), 191.6 (*C*HO), 198.8 [br, $Co_2(CO)_6$] ppm.

Elution with pentane/EtOAc (60:40) and evaporation afforded the triarylated alcohol **14b** (0.240 g, 52%), the data for which are listed below. IR ($CDCl_3$): ν_{O-H} = 3462 (m) cm^{-1}; ν_{sp2C-H} = 3003 (m), 2960 (s), 2939 (s) cm^{-1}; ν_{sp3C-H} = 2839 (m) cm^{-1}; $\nu_{CoC\equiv O}$ = 2080 (s), 2045 (vs), 2004 (vs) cm^{-1}; $\nu_{aromaticC=C}$ = 1607 (s), 1466 (s), 1456 (s) cm^{-1}; other bands at 1330 (m), 1227 (s), 1205 (s),1153 (s), 1126 (s), 1063 (m), 1041 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 837 ([MH − H_2O]$^+$), 809 ([MH − H_2O − CO]$^+$), 781 ([MH − H_2O − 2CO]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.73, 3.75, 3.76, 3.78, 3.83 and 3.86 (6 s, 27 H, *o*- and *p*-OCH_3), 4.77 (d, $^3J_{H,H}$ = 6.0 Hz, O*H*), 6.11 and 6.13 (2 s, 6 H, *m*-C*H* of the Tmp units), 6.65 (s, C*H*Tmp$_2$), 6.73 (d, $^3J_{H,H}$ = 6.0 Hz, C*H*OH) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 36.9 (d, $^1J_{C,H}$ = 131.6 Hz, Ar_2CH), 54.1 (q, $^1J_{C,H}$ = 144.2 Hz, *o*-C−OCH_3), 55.1 (q, $^1J_{C,H}$ = 143.5 Hz, *o*-C−OCH_3), 55.2 (q, $^1J_{C,H}$ = 143.8 Hz, *p*-C−OCH_3), 55.5 (q, $^1J_{C,H}$ = 144.0 Hz, *o*-C−OCH_3), 55.6 (q, $^1J_{C,H}$ = 143.6 Hz, *p*-C−OCH_3), 68.1 (d, $^1J_{C,H}$ = 147.2 Hz, *C*HOH), 90.4 (dd, $^1J_{C,H}$ = 159.3, $^3J_{C,H}$ = 3.1 Hz, *m*-*C*H in TmpCHOH), 90.8 (dd, $^1J_{C,H}$ = 157.9, $^3J_{C,H}$ = 4.1 Hz, *m*-*C*H in Tmp$_2$CH), 91.2 (dd, $^1J_{C,H}$ = 158.9, $^3J_{C,H}$ = 4.7 Hz, *m*-*C*H in Tmp$_2$CH), 100.7 (s, ≡*C*−CHTmp$_2$), 103.51 (d, $^2J_{C,H}$ = 14.0 Hz, ≡*C*−CHOHTmp), 111.09, 112.48 and 114.85 (3 m, *ipso*-*C* of the Tmp units), 158.8, 159.3 (br), 159.7, 160.5 (4 signals, *C*−OMe), 200.60 [s, $Co_2(CO)_6$] ppm.

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