



2,5-Bis(diphenylmethylene)-3-cyclopentenone: a solvent-dependent cobalt cluster mediated propargyl radical coupling process

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Received 26 February 2002; revised 3 April 2002; accepted 8 April 2002

Abstract—Protonation of (1,1-diphenyl-2-propyn-1-ol) $\text{Co}_2(\text{CO})_6$ with HBF_4 in dichloromethane generates the expected metal-stabilized propargyl cation, and also rearranges to give the tricobalt cluster $\text{Ph}_2\text{C}=\text{CH}-\text{CCo}_3(\text{CO})_9$ **9**. In contrast, use of THF as solvent affords the radical $(\text{Co}_2(\text{CO})_6)[\text{HC}\equiv\text{C}-\text{CPh}_2]^\bullet$ **2**, which dimerizes at the methyne position; subsequent cyclization and carbonylation yields 2,5-bis-(diphenylmethylene)-3-cyclopentenone **11**. The products have been characterized by X-ray crystallography, and the scope and mechanism of the reaction are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

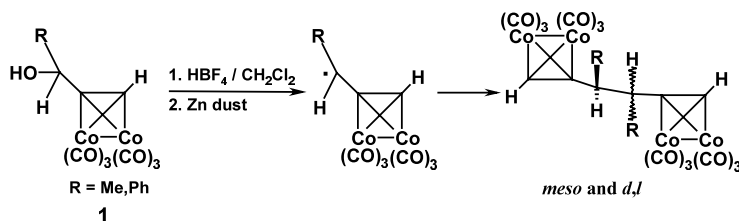
While cobalt-stabilized cations derived from (propargyl alcohol) $\text{Co}_2(\text{CO})_6$ clusters, **1**, are well-characterized and have been extensively exploited for synthetic purposes,¹ the corresponding radical chemistry is less well developed.² In preliminary studies, Nicholas and Melikyan³ have generated coupling products via zinc reduction of the cations, as exemplified in Scheme 1.

Recently, Melikyan⁴ has noted that generation of the cobalt-stabilized cations in certain solvents, notably THF or ether, results in electron transfer to yield the same coupling products as were produced by the zinc reduction procedure. Intrigued by these reports, we chose to generate the radical $(\text{Co}_2(\text{CO})_6)[\text{HC}\equiv\text{C}-\text{CPh}_2]^\bullet$ **2** to see whether it would couple to yield the corresponding symmetrical ethane **3**, or rather mimic the classic behavior⁵ of the triphenylmethyl radical **4**, which for steric reasons yields the unsymmetrical dimer **5**, as in Scheme 2.

2. Results and discussion

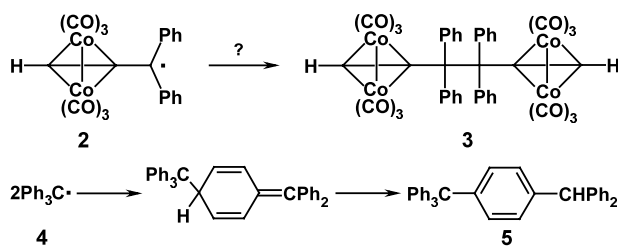
Treatment of $(\text{Co}_2(\text{CO})_6)[\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}]$, **6**, with HBF_4 in SO_2 yields the isolable cation $(\text{Co}_2(\text{CO})_6)-[\text{HC}\equiv\text{C}-\text{CPh}_2]^+$.⁶ In contrast, an earlier report on the protonation of $(\text{Co}_2(\text{CO})_6)[\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}]$ with concentrated sulfuric acid suggests that the major product is the tricobalt cluster **7**. This product was characterized by microanalysis, but no spectroscopic data were given.^{7,8} It is, of course, well established that terminal alkyne complexes of the type $[\text{RC}\equiv\text{CH}](\text{Co}_2(\text{CO})_6)$ rearrange in acid media to yield the corresponding $\text{RCH}_2-\text{CCo}_3(\text{CO})_9$ clusters⁹ (Scheme 3). One might therefore have anticipated the formation of the alcohol **8**, or its elimination product **9**, rather than the saturated cluster **7**. Indeed, we find that treatment of $(\text{Co}_2(\text{CO})_6)[\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}]$ with HBF_4 in dichloromethane at -78°C does yield the alkenyl cluster **9**, and its X-ray structure appears as Fig. 1.

However, returning to our stated objective of generating the radical **2**, the precursor alcohol was treated with

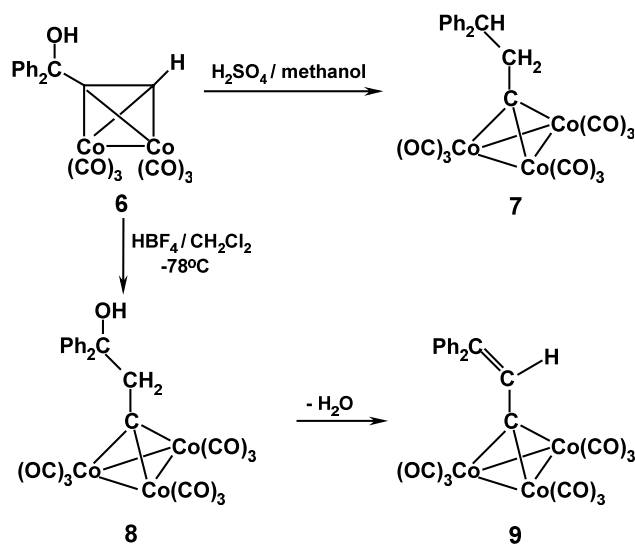


Scheme 1.

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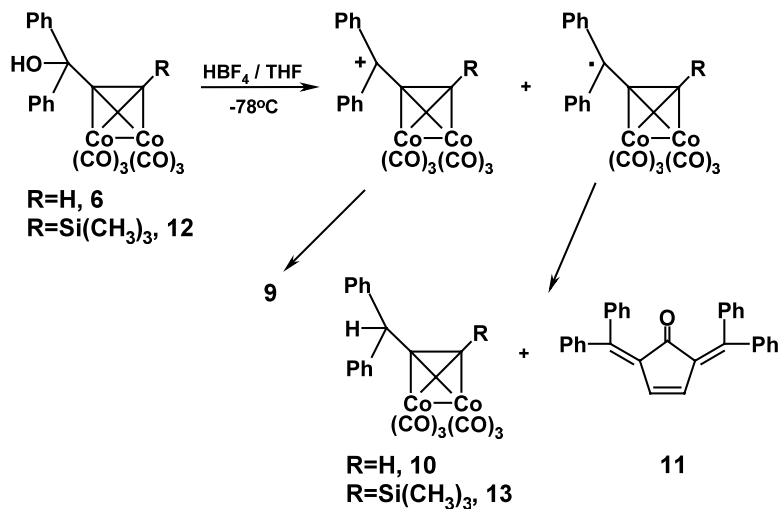


Scheme 2.

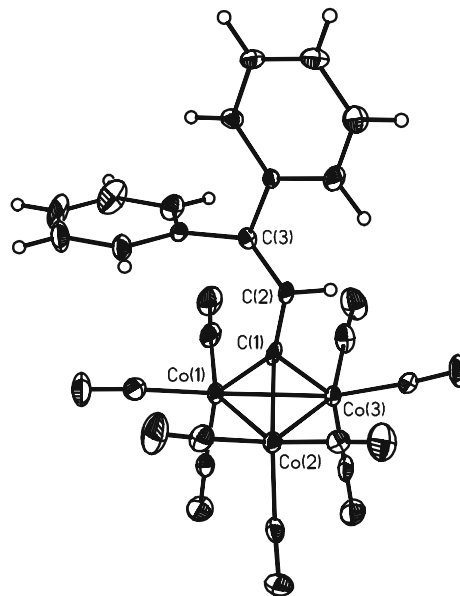


Scheme 3.

HBF₄ in THF at -78°C and the mixture was allowed to warm slowly to room temperature before quenching with water. Chromatographic separation yielded three products: the alkenyl tricobalt cluster **9** (18%), (ethynyldiphenylmethane)Co₂(CO)₆ **10** (8%), and a bright yellow material **11** (28%). The cluster **9** has already been discussed and **10** is readily envisaged as arising either through hydrogen abstraction by the intermediate radical, or hydride transfer to the initially generated cation, as in Scheme 4.



Scheme 4.

Figure 1. Molecular structure of **9**.

The bright yellow compound exhibited a strong infrared absorption at 1703 cm⁻¹, and ¹H and ¹³C NMR resonances typical of carbonyl, phenyl and alkene fragments. The parent peak in the mass spectrum at *m/z* 410, together with the observed breakdown pattern, corresponded to a molecule containing two Ph₂C-C≡CH moieties plus a carbonyl group. Comparison of these data with those of related systems^{10,11} suggested that the yellow compound, **11**, was 2,5-bis-(diphenylmethylene)-3-cyclopentenone, and this assignment was confirmed by X-ray crystallography (Fig. 2).

One might speculate that, since coupling of the diphenylmethyl radicals to give **3** is presumably sterically disfavored, coupling of the methyne termini followed by a carbonyl insertion process could lead to the observed diarylidene. The precise nature of the cobalt center in Scheme 5, which may be mono- or poly-metallic, remains unknown at present, but mechanistic investigations are continuing.

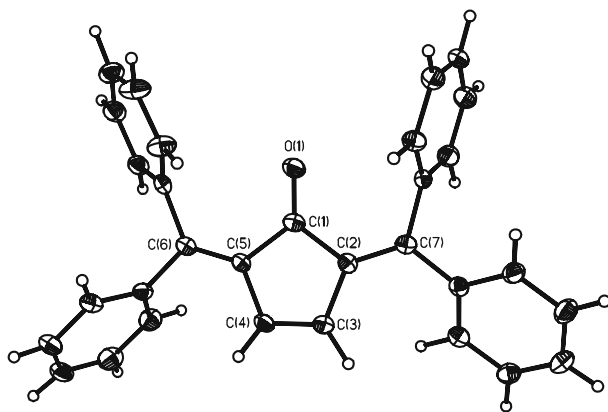
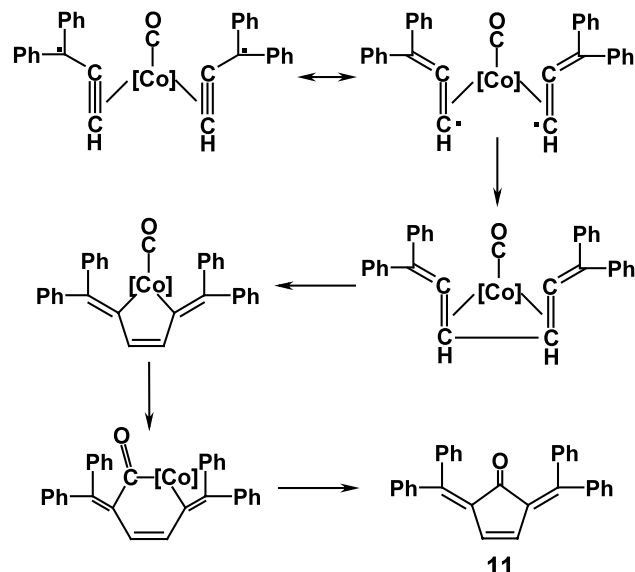


Figure 2. Molecular structure of **11**.

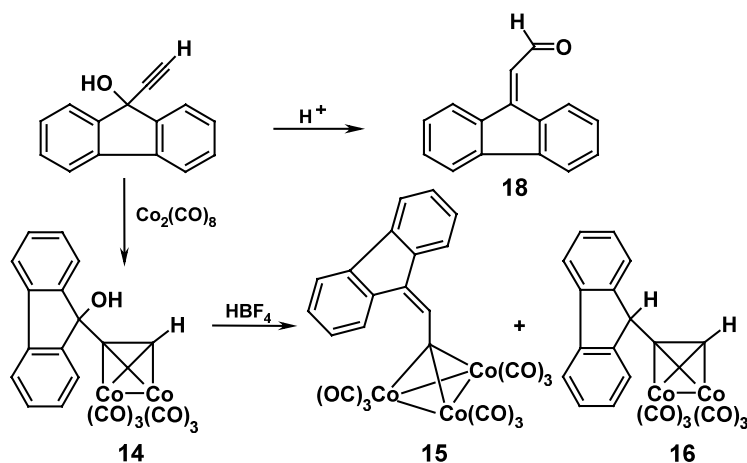
In seeking precedents for such a process, we note Eaton's elegant [4+1] iron-catalyzed cycloaddition of conjugated diallenes and a carbon monoxide to produce five-membered rings.¹² However, in those examples, one must first synthesize the diallene either (a) by dibromocarbene addition to an appropriate butadiene followed by debromination with methyllithium,^{13a} or (b) by palladium-catalyzed coupling of a propargyl bromide and an allenyl-zinc reagent.^{13b} In the present case, it is apparent that the coupling, cyclization and carbonylation processes are all cobalt-mediated in a one-pot synthesis.

Interestingly, protonation of the analogous trimethylsilyl protected cobalt-complexed alkynol **12**, in THF at -78°C , affords only the hydrogen abstraction product **13**, shown in Scheme 4. The diarylidene product is presumably not generated because of the steric interference introduced by the trimethylsilyl group.



Scheme 5.

In an attempt to explore the generality of this process, the corresponding deprotected fluorenyl system **14**, was protonated initially in dichloromethane and diethyl ether and latterly in tetrahydrofuran. The former reaction yielded only a single product, the tricobalt cluster **15**. In contrast, protonation in diethyl ether, which would be expected to generate radicals, yields a reduced quantity of the tricobalt cluster **15**, along with the hydrogen abstraction product **16**, while utilizing THF afforded **16** as the major product (Scheme 6). We surmise that **17**, the fluorenyl analogue of **11**, would suffer severe steric problems and that the fluorenyl moieties would need to be noticeably twisted out of plane, as in the semi-empirically derived model (AM1 Hamiltonian)¹⁴ depicted in Fig. 3.



Scheme 6.

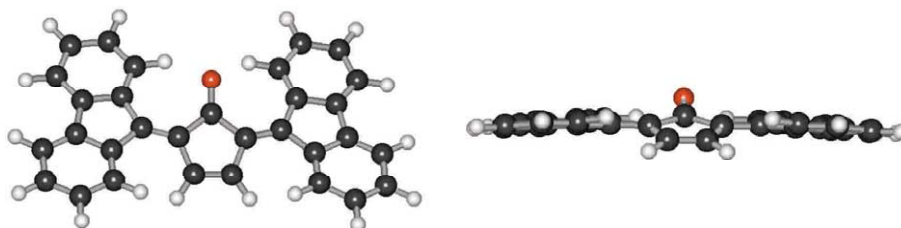


Figure 3. Optimized structural model of **17**.¹⁵

These results contrast markedly with the behavior of the free ligands 1,1-diphenyl-2-propyn-1-ol and 9-ethynylfluorene-9-ol which undergo the Meyer–Schuster (rather than the Rupe)¹⁵ rearrangement to 3,3-diphenylacrolein and 9*H*-fluorene-9-ylideneacetaldehyde **18**, respectively, under acidic conditions (Scheme 6).¹⁶

To conclude, we describe the novel cobalt carbonyl mediated transformation of two propargyl units and a carbon monoxide into a bis-methylene-3-cyclopentenone, which had previously been available only via a multi-step route.¹¹ We are presently investigating the scope and generality of this reaction, and hope to elucidate the mechanism in some detail.

3. Experimental

Treatment of **6**^{6,7} (1.00 g, 2.02 mmol) in CH₂Cl₂ (40 mL) with HBF₄ (0.4 mL, 2.71 mmol) at –78°C in a dry ice/isopropanol bath, afforded **9** (41%, 0.34 g, 0.55 mmol). The analogous reaction in Et₂O (40 mL) gave **9** (34%, 0.28 g, 0.45 mmol) and (ethynyl-diphenylmethane)Co₂(CO)₆ **10** (2%, 0.02 g, 0.04 mmol), while in THF (40 mL), the products were **9** (18%, 0.15 g, 0.24 mmol) **10** (8%, 0.08 g, 0.16 mmol) and 2,5-bis(diphenylmethylene)-3-cyclopentenone **11**,¹¹ (28%, 0.12 g, 0.28 mmol). Each reaction was monitored to completion using thin-layer chromatography, before the solution was allowed to warm to room temperature and quenched with H₂O. All products were extracted with Et₂O, dried over MgSO₄, and flash chromatographed with a 2:1 mixture of hexanes/CH₂Cl₂. **9**: dark red crystals, mp 132–133°C. ¹H NMR (200.20 MHz, CDCl₃): δ 8.25 (1H, s, [C=CH]), 7.40–7.21 (10H, m, [Ph's]). ¹³C NMR (50.35 MHz, CDCl₃): δ 199.8 (Co–CO's), 149.1, 142.7, 139.5, 136.6, 130.2, 128.8, 128.5, 127.9, 127.8, 127.6. Mass spec. (DEI, *m/z* (%)): 536 (23) ([M–3CO]⁺), 452 (25) ([M–6CO]⁺), 368 (42) ([M–9CO]⁺), 191 (42) ([M–Co₃(CO)₉]⁺). (CI, NH₃, *m/z* (%)): 621 (25) ([M+H]⁺), 192 (100) ([M+H–C–Co₃(CO)₉]⁺). Anal. calcd for C₂₄H₁₁O₉Co₃: C, 46.48; H, 1.79. Found: C, 46.08; H, 1.90%. (Ethynyl-diphenylmethane)Co₂(CO)₆, **10**, dark red solid, mp 121–122°C. ¹H NMR (200.20 MHz, CDCl₃): δ 7.46–7.18 (10H, m, [Ph's]), 6.40 (1H, s, [CCH]), 5.32 (1H, s, [Ph₂CH]). ¹³C NMR (50.35 MHz, CDCl₃): δ 199.7 (Co–CO's), 144.0, 128.7, 127.9, 127.2 (Ar C's), 73.4 (CCH), 57.8 (Ph₂CH). Mass spec. (DEI, *m/z* (%)): 450 (39) ([M–CO]⁺), 394 (100) ([M–3CO]⁺), 310 (44) ([M–6CO]⁺), 251 (37) ([M–Co–6CO]⁺). (CI, NH₃, *m/z* (%)): 451 (47) ([M+H–CO]⁺), 310 (36) ([M–6CO]⁺), 192 (31) ([M–Co₂(CO)₆]⁺). Anal. calcd for C₂₁H₁₂O₆Co₂·H₂O: C, 50.83; H, 2.84. Found: C, 50.82; H, 2.86%.

Addition of Co₂(CO)₈ (1.83 g, 5.4 mmol) to trimethylsilyl(1,1-diphenyl-2-propyn-1-ol)¹⁷ (1.50 g, 5.4 mmol) in 40 mL of tetrahydrofuran afforded trimethylsilyl(1,1-diphenyl-2-propyn-1-ol)Co₂(CO)₆ **12**, as a dark red solid (88%, 2.67 g, 4.7 mmol). ¹H NMR (200.20 MHz, CDCl₃): δ 7.68–7.63 (4H, m, [Ph's]), 7.35–7.19 (6H, m, [Ph's]), 2.71 (1H, s, [OH]), 0.45 (9H, s, [SiCH₃]₃). ¹³C NMR (50.35 MHz, CDCl₃): δ 199.8 (Co–CO's), 146.6,

128.0, 127.6, 126.3 (Ar C's), 80.6 (COH), 78.3 (CCH). Mass spec. (DEI, *m/z* (%)): 538 (3) ([M–CO]⁺), 398 (17) ([M–6CO]⁺), 280 (14) ([M–Co₂(CO)₆]⁺), 263 (91) ([M–OH–Co₂(CO)₆]⁺). (CI, NH₃, *m/z* (%)): 522 (4) ([M+H–OH–CO]⁺), 455 (4) ([M+H–4CO]⁺), 398 (5) ([M–6CO]⁺), 263 (100) ([M–OH–Co₂(CO)₆]⁺).

Treatment of **12**, (1.55 g, 2.74 mmol) with HBF₄ (0.4 mL, 2.94 mmol) in tetrahydrofuran (40 mL) afforded, (trimethylsilylethynyl-diphenylmethane)Co₂(CO)₆ **13**, as a black solid, (65%, 0.98 g, 1.8 mmol), mp 91–93°C. ¹H NMR (300.13 MHz, CDCl₃): δ 7.58–7.55 (4H, m, [Ph's]), 7.41–7.30 (6H, m, [Ph's]), 5.46 (1H, s, [Ph₂CH]), 0.47 (9H, s, [Si(CH₃)₃]). ¹³C NMR (75.48 MHz, CDCl₃): δ 200.0 (Co–CO's), 143.9, 128.6, 128.2, 127.3 (Ar C's), 115.4 (CCH), 78.7 (CCH), 59.8 (Ph₂CH). Mass spec. (DEI, *m/z* (%)): 466 (10) ([M–3CO]⁺), 382 (13) ([M–6CO]⁺), 264 (4) ([M–Co₂(CO)₆]⁺). (CI, NH₃, *m/z* (%)): 383 (3) ([M+H–6CO]⁺), 265 (23) ([M+H–Co₂(CO)₆]⁺).

Treatment of **14**,¹⁸ (1.00 g, 2.03 mmol) with HBF₄ (0.4 mL, 2.71 mmol) in dichloromethane (40 mL) yielded the fluorenylidene–tricobalt cluster **15**, as a black solid (38%, 0.32 g, 0.51 mmol), mp 141–142°C. ¹H NMR (200.20 MHz, CDCl₃): δ 8.94 (1H, s, [C=CH]), 8.11 (1H, d, [Ar]), 7.77–7.70 (3H, m, [Ar]), 7.45–7.29 (4H, m [Ar]). ¹³C NMR (50.35 MHz, CDCl₃): δ 199.8 (Co–CO's), 148.4, 141.3, 140.4, 139.2, 136.3, 129.7, 128.8, 128.4, 128.3, 127.2, 126.0, 120.3, 120.1. Mass spec. (DEI, *m/z* (%)): 590 (1) ([M–CO]⁺), 450 (7) ([M–6CO]⁺), 178 (100) ([M–C–Co₃(CO)₉]⁺). (CI, NH₃, *m/z* (%)): 619 (5) ([M+H]⁺), 591 (3) ([M+H–CO]⁺), 366 (10) ([M–9CO]⁺), 179 (100) ([M+H–C–Co₃(CO)₉]⁺). Repetition of this reaction in 40 mL of diethyl ether afforded **15** (23%, 0.19 g, 0.31 mmol), and (9-ethynylfluorene)Co₂(CO)₆ **16**, as a dark red solid (7%, 0.07 g, 0.14 mmol), mp 98°C. ¹H NMR (500.13 MHz, CDCl₃): δ 7.78–7.69 (4H, d of d, [Ar]), 7.45–7.34 (4H, m [Ar]), 6.38 (1H, s, [CCH]), 5.13 (1H, s, [CHCCH]). ¹³C NMR (125.77 MHz, CDCl₃): δ 199.3 (Co–CO's), 146.7, 140.6, 128.2, 127.4, 125.1, 120.2 (Ar C's), 98.6 (CCH), 74.9 (CCH), 49.7 (Ar–CH). Mass spec. (DEI, *m/z* (%)): 308 (100) ([M–6CO]⁺), 249 (25) ([M–Co–6CO]⁺). (CI, NH₃, *m/z* (%)): 449 (42) ([M+H–CO]⁺), 308 (100) ([M–6CO]⁺), 249 (13) ([M–Co–6CO]⁺). Addition of HBF₄ (0.4 mL, 2.71 mmol) to **14** (1.0 g, 2.03 mmol) in THF (40 mL), afforded **15** (10%, 0.08 g, 0.13 mmol) and **16** (30%, 0.29 g, 0.61 mmol).

X-Ray crystal data for **9**: C₂₄H₁₁O₉Co₃, dark red plate (0.08×0.28×0.34 mm), monoclinic, *C*2/*c*, *a* = 16.793(4), *b* = 7.874(2), *c* = 36.834(8) Å, β = 96.923(4)°, *V* = 4834.6(19) Å³, *Z* = 8, ρ_{calcd} 1.704 g cm^{–3}, *T* = 197(2) K, μ = 2.086 mm^{–1}; *R*₁ = 0.0612, *wR*₂ = 0.1294 (based on *F*²) for 326 variables and 16663 reflections (4236 independent); *R*_{int} = 0.1102, with *I* > 2σ(*I*) and 1.11 < θ < 24.99.

X-Ray crystal data for **11**: C₃₁H₂₂O, yellow rod (0.04×0.05×0.40 mm), orthorhombic, *P*2₁2₁2₁, *a* = 5.9605(15), *b* = 12.804(3), *c* = 28.760(8) Å, *V* = 2194.9(10) Å³, *Z* = 4, ρ_{calcd} 1.242 g cm^{–3}, *T* = 197(2) K, μ = 0.073 mm^{–1}; *R*₁ = 0.0514, *wR*₂ = 0.0909 (based on *F*²) for 378 variables and 16498 reflections (3849 independent); *R*_{int} = 0.0927 with *I* > 2σ(*I*) and 1.42 < θ < 25.00.

Crystallographic data (excluding structure factors) for the molecules reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 180385 (**9**) and 180386 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Financial Support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. J.H.K. thanks NSERC and the Province of Ontario for graduate scholarships. Mass spectra were acquired courtesy of Dr. Kirk Green of the McMaster Regional Mass Spectrometry Center.

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