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Organometallic derivatives of natural products: dicobalt hexacarbonyl complexes of geranyl-alkynes

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Abstract: Treatment of methyl geranyl ether with diiron nonacarbonyl leads to hydrogen migration to form previously unknown *E* and *Z* 1-methoxy-3,7-dimethyl-1,6-octadiene in low yield. Sodium propargyl alkoxide and geranyl bromide yield propargyl geranyl ether, **13**; subsequent reaction with dicobalt octacarbonyl and then bis(diphenylphosphino)methane furnishes the corresponding alkyne-$Co_2(CO)_4$(dppm) tetrahedral cluster, **16**. Reaction of geranylacetone with phenylethynyl-lithium, and then with $Co_2(CO)_8$, forms (1-phenyl-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol)$Co_2(CO)_6$, **19**. The carbynyltricobaltnonacarbonyl clusters $RC(=O)CCo_3(CO)_9$, where R = geranyl, **22**, or farnesyl, **25**, are preparable in very good yield either by reaction of the appropriate alcohol with trichloroacetyl chloride and then $Co_2(CO)_8$, or by reaction with the metal-stabilized acylium ion $[Co_3(CO)_9C{=}C{=}O]^+$, **24**. Potential use of these (η^2-alkyne)dicobalt complexes in Pauson-Khand or Nicholas cyclizations is discussed.

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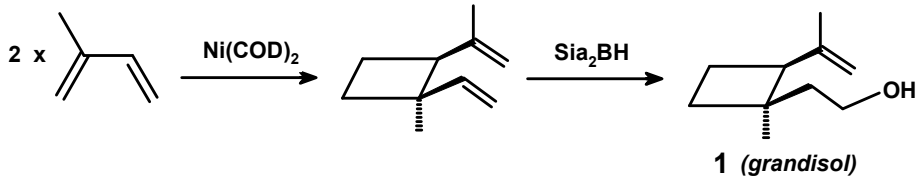
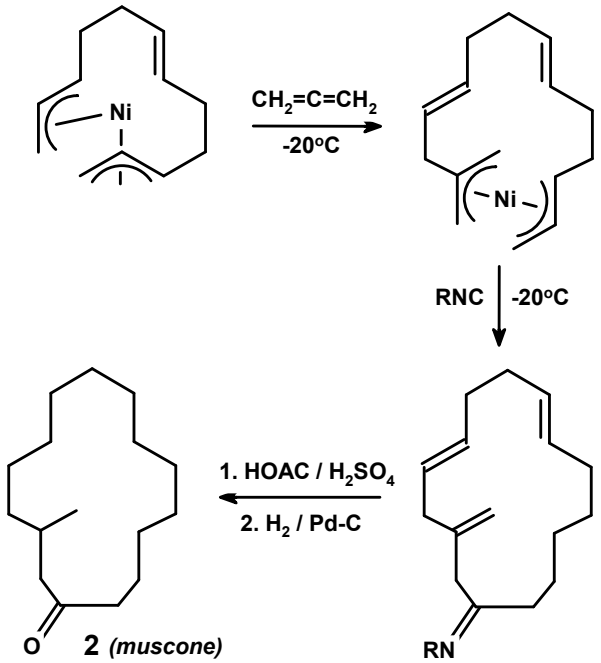
Introduction

In continuation of our studies on organometallic derivatives of natural products, such as steroids (both estrogenic[1] and androgenic[2]), terpenes (menthol,[3] camphor,[4] fenchone,[5] verbenone[6]) or chalcones,[7] we here report syntheses of cobalt carbonyl complexes containing the geranyl group. The use of organometallic reagents in the syntheses of natural products has a long and distinguished pedigree. Particularly fine examples include Billups' nickel-catalyzed dimerization of isoprene and subsequent conversion to *grandisol*, **1**, a boll weevil pheromone (Scheme 1),[8] Baker's preparation of *muscone*, **2**, from (1,5,9-cyclododeca-triene)nickel (Scheme 2),[9] and Vollhard's elegant cobalt-mediated route to *estrone*.[10]



Scheme 1. Nickel-mediated synthesis of (±)-*grandisol*, **1**.



Scheme 2. Organometallic route to (±)-*muscone*, **2**.

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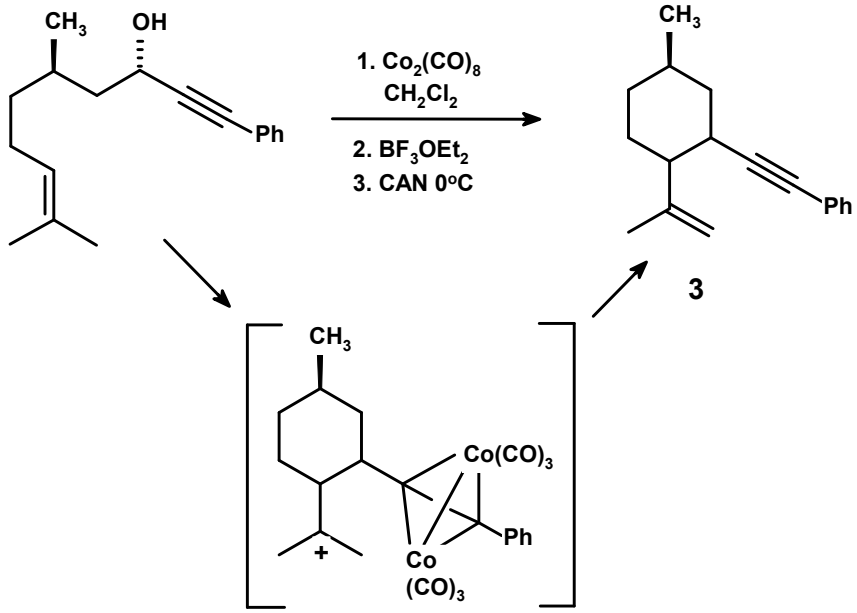
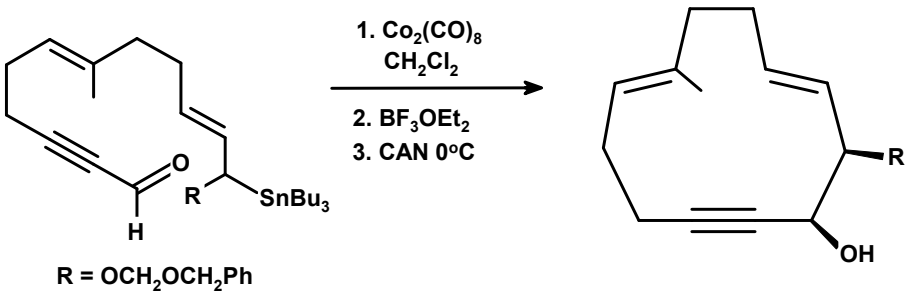
Since geranyl pyrophosphate is the precursor to a wide variety of monoterpenes whose syntheses proceed via cyclizations on enzyme templates leading to very specific, often chiral, products,[11] one might envisage the folding of a geranyl (or even a farnesyl) unsaturated chain on a transition metal template, thus leading to a single product in a controlled fashion. A recent closely related example of such a process (Scheme 3) is Tyrrell's cyclization of an alkynyl dicobalt-hexacarbonyl derivative of citronellol to form 2-phenylethynyl-1-isopropenyl-4-methylcyclohexane, **3**, a near relative of menthene.[12] Likewise, in earlier work, Marshall[13] used this approach to prepare a cyclododecadienynol, as shown in Scheme 4.



Scheme 3. Cobalt-mediated cyclization of an alkynyl-citronellol to form **3**.



Scheme 4. Cobalt-mediated cyclization to form a cyclododecadienynol.

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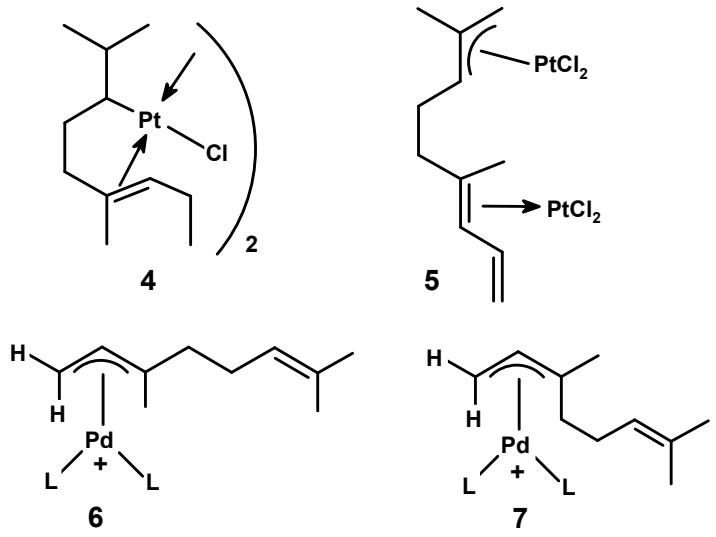
Pioneering work by Schwartz and Dunn[14] involved the reaction of geranyl (and farnesyl) methyl ether with K_2PtCl_4 to form complexes tentatively assigned as **4** and **5** (Scheme 5). In a subsequent study by Åkermark and Vitagliano, it was reported that cationic (η^3-geranyl)- and (η^3-neryl)-palladium complexes, **6** and **7**, respectively, undergo nucleophilic attack to yield initially linalyl-amines that subsequently isomerize to a mixture of geranyl- and neryl-amines.[15]



Scheme 5. Selected geranyl and neryl platinum and palladium complexes.

We here report syntheses of cobalt carbonyl complexes of prop-2-ynyl geranyl ether, of geranyl acetate, and of the phenylethynyl adduct to geranyl-acetone.

Results and discussion

Reaction of geranyl methyl ether with diiron nonacarbonyl

Initially, it was decided to study the reaction of geranyl methyl ether, **8**, with iron carbonyl to see whether the diene would yield an η^4-$Fe(CO)_3$ complex that could be further elaborated. When the ether **8** was stirred for 48 h. at room temperature with $Fe_2(CO)_9$ in THF then at reflux for a further 3 d, and the products separated by chromatography on silica, two

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organic products, **9** and **10**, were isolated in very low (5%) yield. There was also a trace of an iron complex exhibiting carbonyl infrared absorptions at 2036 and 1963 cm^{-1}; however, its existence was fleeting and isolation was not possible. The products **9** and **10** were shown to be the *cis* and *trans* isomers, respectively, of previously unknown 1-methoxy-3,7-dimethyl-1,6-octadiene whereby the C(2)=C(3) double bond has migrated so as to form the corresponding pair of vinyl ethers (Scheme 6).[16] The closest analogues of **9** and **10** of which we are aware are the *E* and *Z* isomers of methyl 2,6-dimethyl-1-hepten-6-yl ether, **11**, made by the Wittig reaction of 6-methyl-5-hepten-2-one with Ph_3P=C(H)OMe (Scheme 7).[17]

One can readily envisage the intermediacy of an allyl iron hydride, **12**, a well-established mechanistic scenario.[18] These isomers were unambiguously identified from their ^{1}H and ^{13}C NMR spectra. In particular, the doublet character of the ^{1}H resonance for the 10-methyl group revealed the presence of a hydrogen now attached to C(3); the identities of the *Z* and *E* isomers, **9** and **10**, were evident from the $^3J(H_1\text{-}H_2)$ coupling constants of 6 Hz and 13 Hz, respectively, entirely typical values for vinyl methyl ethers.[19] Although the overall isomerization yield is very low, it is interesting since this molecular rearrangement in some ways parallels the migration of pyrophosphate from C(1) to C(3) in the conversion of geranyl- to linalyl-pyrophosphate that is a key feature of the enzyme-mediated pathway to monoterpenes such as menthol, camphor and many others.[11] However, in this case, it is a hydrogen atom rather than the methoxy (or pyrophosphate) substituent that undergoes migration from C(1) to C(3).

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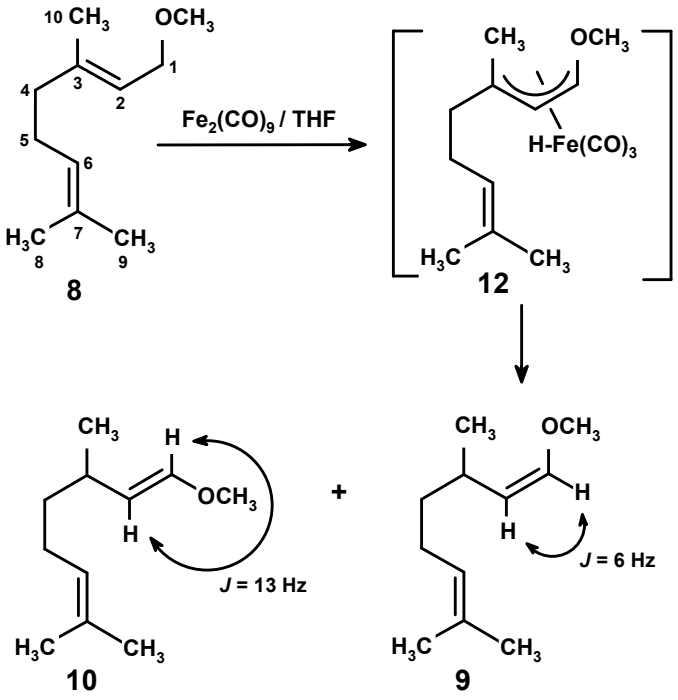
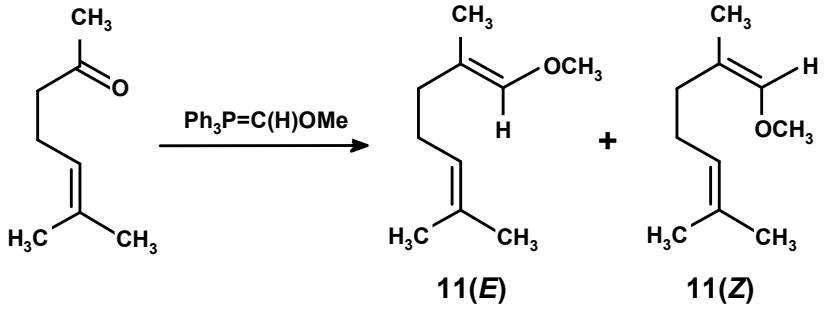


Scheme 6. Iron carbonyl mediated isomerization of geranyl methyl ether.



Scheme 7. Schlosser's route to methyl 2,6-dimethyl-1-hepten-6-yl ether, **11**.

Syntheses of dicobalt-hexacarbonyl and tricobalt-nonacarbonyl geranyl derivatives

The reaction of sodium propargyl alkoxide with geranyl bromide furnished propargyl geranyl ether, **13**, in 75% yield. Subsequent treatment with dicobalt octacarbonyl in THF gave the cobalt complex, **14**, as a maroon oil in 78% yield. This system may be appropriate for a Pauson-Khand cyclization[20] to form the corresponding cyclopentenone, **15**, and work in this area is continuing.

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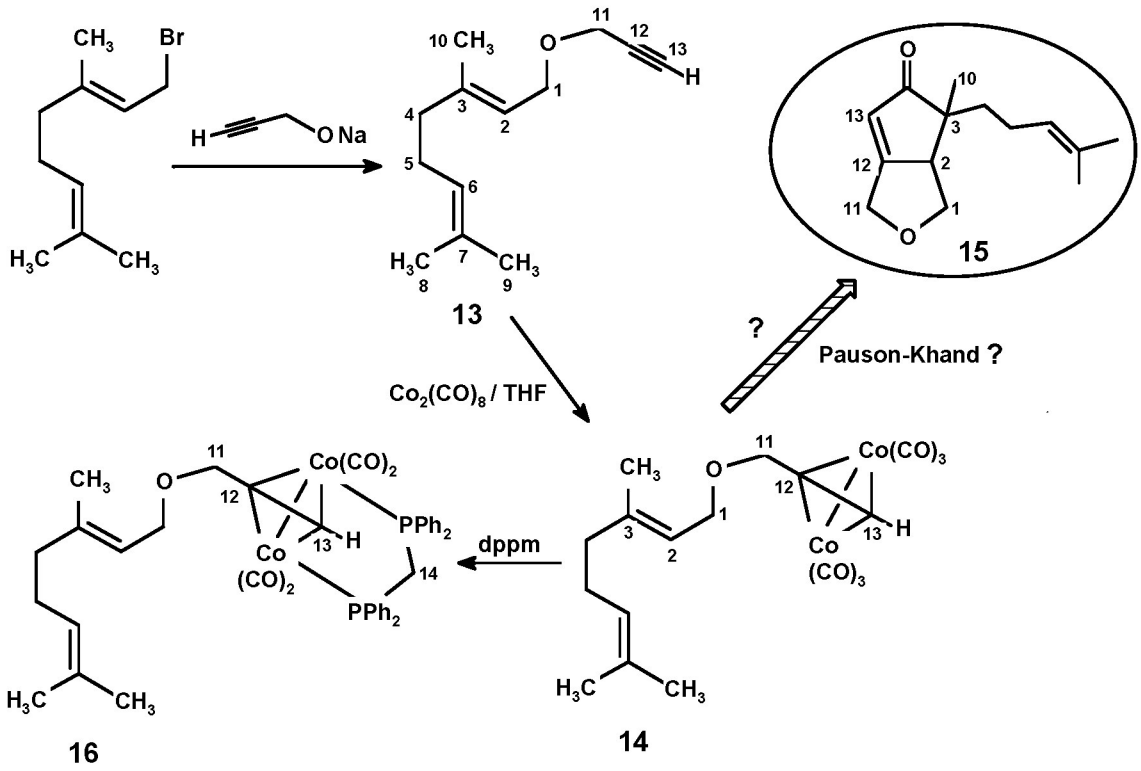

Scheme 8. Reactions of propargyl geranyl ether, **13**.

With the aim of obtaining a sample suitable for an X-ray crystallographic structural determination, the alkyne-$Co_2(CO)_6$ cluster, **14**, was allowed to react with bis(diphenylphosphino)methane (dppm) and gave the desired complex, **16**, in 30% yield, again as a maroon oil. The products shown in Scheme 8 were characterized by ^{1}H and ^{13}C NMR spectroscopy and electrospray mass spectrometry.

We also wished to prepare molecules with the potential to undergo a Nicholas-type reaction[21] via a cobalt-stabilized carbocation, and so phenylethynyl-lithium was added to a THF solution of geranyl-acetone, which also contained approximately 35% neryl-acetone (from which it can be separated only with difficulty). The geranyl and neryl adducts, **17** and **18**, shown in Schemes 9 and 10, were then treated with dicobalt octacarbonyl to form the alkyne-$Co_2(CO)_6$ complexes **19** and **20**, respectively, in a total yield of 69%. At this stage, after multiple chromatographic separations, it was possible to obtain a clean sample of the

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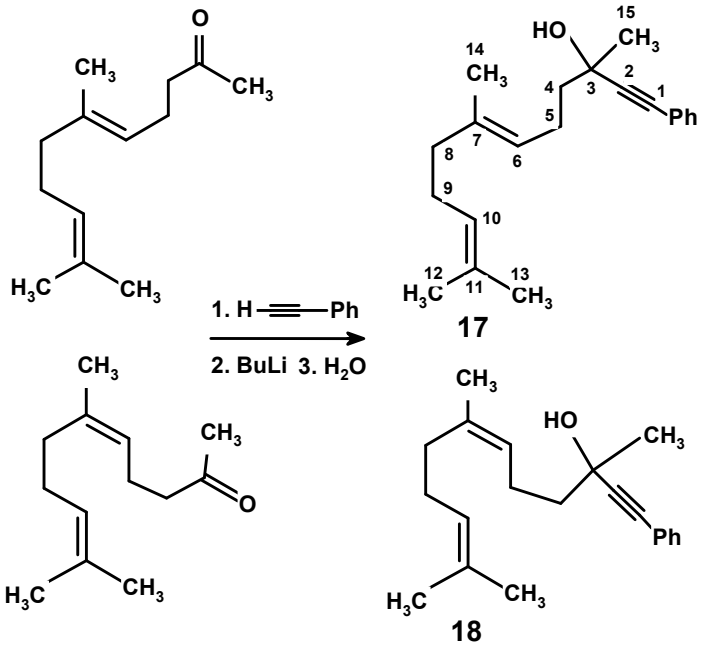
major isomer and it was found to be the geranyl complex, **19**, as revealed by its ^{13}C NMR spectrum. Although the geranyl and neryl frameworks exhibit similar NMR spectra, there is a characteristic difference in the ^{13}C chemical shift of C(4); in the geranyl system this is found at 39-40 ppm, whereas in the corresponding neryl analogues this peak is in the range 32-35 ppm.[22] In **17** and **18**, the signals for C(8) (which correspond to C(4) in geraniol or nerol) appear at 39.8 and 32.1, respectively, and in the cobalt complex, **19**, the corresponding resonance is also found at 39.8 ppm. Future work will involve protonation of the **19**/**20** mixture in the expectation that the (*Z*) C(2)=C(3) linkage in the minor (neryl) isomer should favour cyclization to form **21**, and so facilitate separation of the products.



Scheme 9. Reaction of geranyl- and neryl-acetone with phenylethynyl-lithium.

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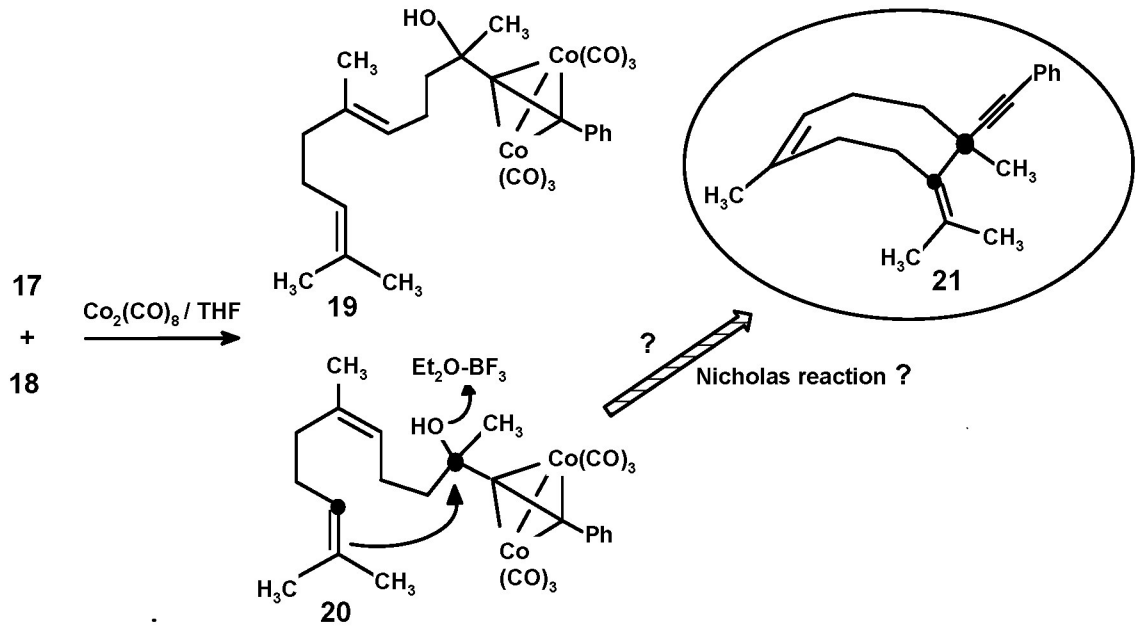
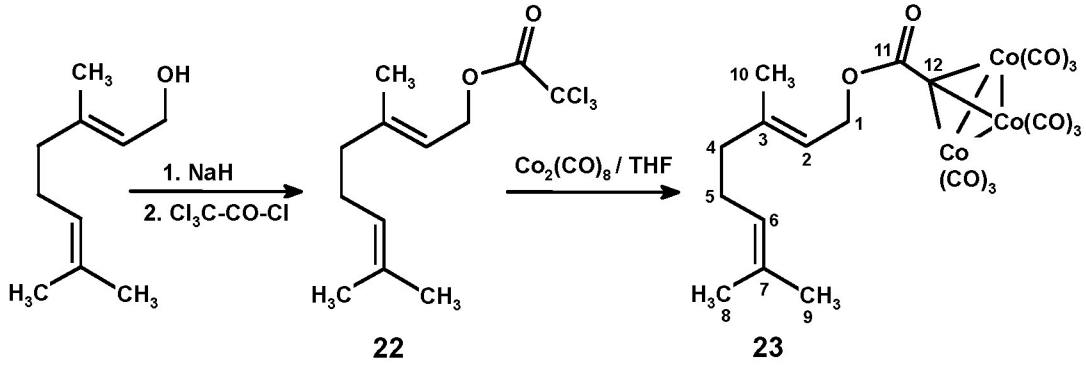


Scheme 10. Cobalt clusters derived from geranyl- and neryl-acetone.

Finally, to form a nonacarbonyltricobalt tetrahedral cluster, the required starting material is an appropriate trichloromethyl derivative,[23] as in geranyl trichloroacetate, **22**. As depicted in Scheme 11, this is readily prepared in 64% yield from trichloroacetyl chloride and sodium geranyl alkoxide. Subsequent reaction with dicobalt octacarbonyl delivered the geranyl tricobalt cluster, **23**, in 42% yield.



Scheme 11. Synthesis of a geranyl-carbynyltricobalt nonacarbonyl cluster (**23**).

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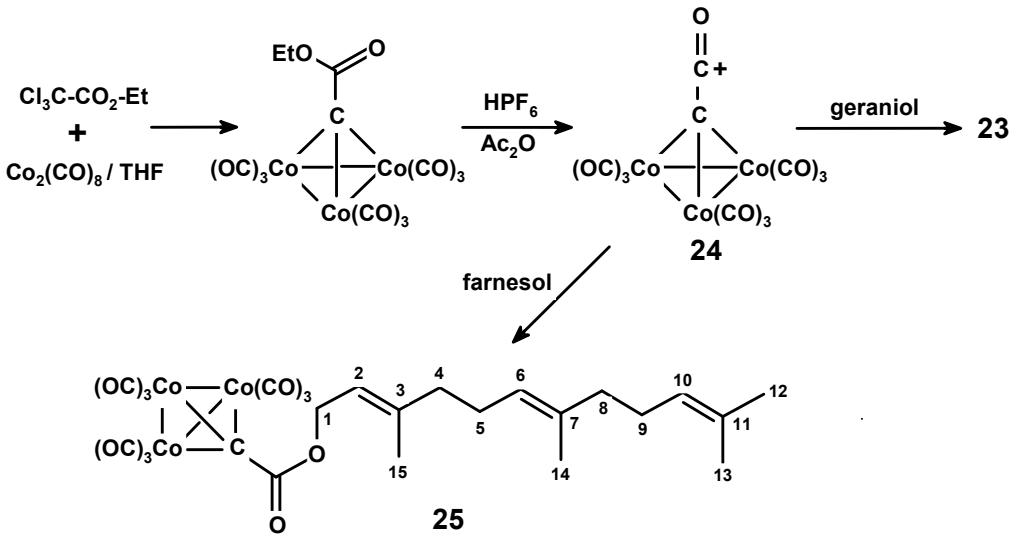
Interestingly, such products are also preparable in better yields by treatment of the metal-stabilized acylium ion, $[Co_3(CO)_9C\text{-}C{=}O]^+$, **24**,[23,24] with geraniol (or farnesol) as depicted in Scheme 12. Indeed, this alternative route furnishes the geranyl ester, **23**, and also the corresponding farnesyl complex, **25**, in 92% and 74% yields, respectively.



Scheme 12. Synthesis of geranyl- (**23**) and farnesyl- (**25**) carbynyltricobalt nonacarbonyl clusters via the cluster-stabilized acylium ion (**24**).

Conclusions

Attachment of an alkynyl functionality to the geranyl (or neryl) chain, and subsequent addition of a dicobalt hexacarbonyl unit to form a tetrahedral Co_2C_2 cluster, yields molecular frameworks appropriate for further elaboration via Pauson-Khand cyclizations or metal-stabilized carbocationic intermediates (Nicholas reactions). In addition, geranyl and farnesyl derivatives of nonacarbonyltricobaltcarbynyl clusters are readily preparable either via reaction of dicobalt octacarbonyl with an appropriately substituted trichloroacetate, or by reaction of geraniol or farnesol with a cobalt-stabilized acylium ion. The chemistry of the geranyl-containing cobalt clusters will be the focus of a future report.

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Experimental

All reactions were carried under a nitrogen atmosphere, and solvents were dried by standard procedures. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Varian VNMRS 400 or 500 MHz spectrometers. Assignments were based on standard 2-dimensional NMR techniques (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC, NOESY). Electrospray mass spectrometry was performed on a Micromass Quattro micro instrument. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Merck silica gel 60 (230-400 mesh) was used for flash chromatography. Geraniol and geranylacetone were obtained from Aldrich, and dicarbonyl octacarbonyl was purchased from Strem Chemicals.

Reaction of geranyl methyl ether with diiron nonacarbonyl. (*E*)-1-Methoxy-3,7-dimethyl-2,6-octadiene (geranyl methyl ether), **8**, (5.00 g, 29.7 mmol), prepared from geraniol, sodium hydride and methyl iodide, was added to dry THF (250 mL) containing diiron nonacarbonyl (10.8 g, 29.7 mmol) and the mixture stirred at room temperature for 2 d, and then at reflux for a further 3 d. After removal of solvent and chromatography on silica using pentane/ dichloromethane as eluent, and recovery of unchanged starting material, two new isomers were isolated in very low yield: (*Z*)-1-methoxy-3,7-dimethyl-1,6-octadiene, **9**, (86 mg, 0.51 mmol; 1.7 %), and (*E*)-1-methoxy-3,7-dimethyl-1,6-octadiene, **10**, (154 mg, 0.92 mmol; 3.1 %). Data for **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (d, J = 6.0 Hz, 1H, H_1), 5.11 (t, J = 5.5 Hz, 1H, H_6), 4.15 (dd, J = 6.0 Hz, J = 7.1 Hz, 1H, H_2), 3.55 (s, 3H, OMe), 2.59 (m, 1H, H_3), 1.95 (m, 2H, $H_{5,5'}$), 1.68 (s, 3H, Me_9), 1.59 (s, 3H, Me_8), 1.26 (m, 2H, $H_{4,4'}$), 0.95 (d, J = 6.9 Hz, 3H, Me_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1 (C_1), 130.9 (C_7), 125.7 (C_6), 113.5 (C_2), 59.4 (OMe), 37.8 (C_4), 28.7 (C_3), 26.0 (C_5), 25.7 (Me_9), 21.3 (Me_{10}), 17.6 (Me_8). Data for **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (d, J = 13.0 Hz, 1H, H_1), 5.11 (t, J = 5.5 Hz, 1H, H_6),

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4.58 (dd, J = 13.0 Hz, J = 8.9 Hz, 1H, H_2), 3.50 (s, 3H, OMe), 2.01 (m, 1H, H_3), 1.95 (m, 2H, $H_{5,5'}$), 1.68 (s, 3H, Me_9), 1.59 (s, 3H, Me_8), 1.26 (m, 2H, $H_{4,4'}$), 0.98 (d, J = 6.9 Hz, 3H, Me_{10}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1 (C_1), 131.1 (C_7), 124.7 (C_6), 109.0 (C_2), 55.8 (OMe), 38.1 (C_4), 32.4 (C_3), 25.8 (C_5), 25.7 (Me_9), 21.1 (Me_{10}), 17.6 (Me_8). (MS ESI): $[M]^+$ calcd for $C_{11}H_{20}O$ 168.1514, found 168.1511.

*(E)-3,7-Dimethyl-1-(prop-2-ynyloxy)octa-2,6-diene (**13**).* Analogously to the literature procedure,[25] sodium hydride (0.16 g, 6.67 mmol) was added to a solution of propargyl alcohol (0.35 mL, 6.01 mmol) in THF (60 mL) at -78 ºC and the mixture was stirred for 1.5 h, and then allowed to warm to room temperature. Upon addition of geranyl bromide (1.10 mL, 5.51 mmol), the solution was allowed to stir for 12 h, then quenched with water (30 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and evaporated to yield a residue that was subjected to flash chromatography to yield **13** (800 mg, 4.16 mmol; 75%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (t, J = 7.0 Hz, 1H, H_2), 5.07 (t, J = 6.5 Hz, 1H, H_6), 4.10 (t, J = 2.5 Hz, 2H, $H_{11,11'}$), 4.07 (d, J = 7.0 Hz, 2H, $H_{1,1'}$), 2.40 (t, J = 2.5 Hz, 1H, C≡CH), 2.08 (dt, J = 6.5 Hz, J = 7.0 Hz, 2H, $H_{5,5'}$), 2.02 (t, J = 7.0 Hz, 2H, $H_{4,4'}$), 1.67 (s, 3H, Me_{10}), 1.66 (s, 3H, Me_9), 1.59 (s, 3H, Me_8). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (C_3), 131.7 (C_7), 124.0 (C_6), 120.0 (C_2), 80.2 (*C*≡CH), 74.2 (C≡*C*H), 66.0 (C_1), 56.7 (C_{11}), 39.7 (C_4), 26.4 (C_5), 25.7 (Me_9), 17.7 (Me_8), 16.5 (Me_{10}).

[*(E)-3,7-Dimethyl-1-(prop-2-ynyloxy)octa-2,6-diene]hexacarbonyldicobalt (**14**).* To a solution of dicobalt octacarbonyl (860 mg, 2.52 mmol) in THF (40 mL) was added a solution of **13** (484 mg, 2.52 mmol) in THF (20 mL) via cannula. The solution was stirred for 24 h at room temperature, becoming a deep red; after removal of the solvent under vacuum, the resulting product was chromatographed on silica using chloroform/cyclohexane as eluent to give **14** as a maroon oil (935 mg, 1.96 mmol; 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06 (s,

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1H, C≡CH), 5.36 (t, J = 6.5 Hz, 1H, H_2), 5.09 (t, J = 6.0 Hz, 1H, H_6), 4.63 (bs, 2H, $H_{11,11'}$), 4.16 (d, J = 6.5 Hz, 2H, $H_{1,1'}$), 2.09 (dt, J = 6.0 Hz, J = 6.5 Hz, 2H, $H_{5,5'}$), 2.04 (t, J = 6.5 Hz, 2H, $H_{4,4'}$), 1.69 (s, 3H, Me_{10}), 1.68 (s, 3H, Me_9), 1.60 (s, 3H, Me_8). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8 (CO's), 140.8 (C_3), 131.8 (C_7), 124.1 (C_6), 120.6 (C_2), 91.7 (*C*≡CH), 72.2 (C≡*C*H), 70.0 (C_{11}), 67.2 (C_1), 39.7 (C_4), 26.5 (C_5), 25.8 (Me_9), 17.8 (Me_8), 16.6 (Me_{10}). IR (CH_2Cl_2) ν(CO) 2094, 2054, 2027 cm^{-1}. (MS ESI): $[M - CO]^+$ calcd for $C_{18}H_{20}O_6Co_2$ 449.9924, found 449.9926.

[*(E)-3,7-Dimethyl-1-(prop-2-ynyloxy)octa-2,6-diene][bis(diphenylphosphino)methane]-tetracarbonyldicobalt (**16**).* To a solution of **14** (214 mg, 0.45 mmol) in THF (20 mL) was added dppm (173 mg, 0.45 mmol), and the mixture was heated at reflux for 16 h, after which time the solution appeared brown-black in colour. Removal of solvent under vacuum and chromatography on silica using chloroform/cyclohexane as eluent gave **16** as a maroon oil (109 mg, 0.14 mmol; 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, $^3J_{H\text{-}P}$ = 4.8 Hz, 4H, phenyl *o*-H), 7.33 (d, $^3J_{H\text{-}P}$ = 5.6 Hz, 4H, phenyl *o*-H), 7.26 (m, 8H, phenyl *m*/*p*-H), 7.15 (m, 4H, phenyl *m*-H), 5.64 (t, $^3J_{H\text{-}P}$ = 4.8 Hz, 1H, C≡CH), 5.40 (t, J = 6.5 Hz, 1H, H_2), 5.11 (t, J = 5.2 Hz, 1H, H_6), 4.80 (m, 2H, $H_{11,11'}$), 4.22 (d, J = 6.5 Hz, 2H, $H_{1,1'}$), 3.52 (m, 1H, H_{14}), 3.37 (m, 1H, $H_{14'}$), 2.11-2.05 (m, 4H, $H_{4,4',5,5'}$), 1.70 (s, 3H, Me_{10}), 1.67 (s, 3H, Me_9), 1.60 (s, 3H, Me_8). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 204.2 (CO's), 139.8 (C_3), 137.5 (d, $^1J_{C\text{-}P}$ = 20 Hz, phenyl *ipso*-C), 136.5 (d, $^1J_{C\text{-}P}$ = 20 Hz, phenyl *ipso*-C), 132.1 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, phenyl *o*-C), 131.8 (C_7), 131.7 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, phenyl *o*-C), 129.6 (phenyl *p*-C), 129.5 (phenyl *p*-C), 128.3 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, phenyl *m*-C), 128.2 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, phenyl *m*-C), 124.2 (C_6), 121.4 (C_2), 95.6 (*C*≡CH), 75.0 (C≡*C*H), 72.9 (C_{11}), 67.0 (C_1), 41.3 (C_{14}), 39.7 (C_4), 26.6 (C_5), 25.8 (Me_9), 17.8 (Me_8), 16.7 (Me_{10}). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.0. IR (CH_2Cl_2) ν(CO) 2021, 1992, 1965 cm^{-1}.

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*(E)- and (Z)-1-Phenyl-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol, (**17**) and (**18**).* In a typical procedure, *n*BuLi (17.7 mL of a 1.6 M hexane solution, 28.3 mmol) was added dropwise to a solution of phenylacetylene (3.1 mL, 28.3 mmol) in THF (250 mL) at -78 ºC and the mixture was stirred for 30 min. The solution was allowed to warm to room temperature and, after 15 min, a 65/35 mixture of geranyl- and neryl-acetone (5.7 mL, 25.7 mmol) was added dropwise over 5 min. The solution was stirred at room temperature for 12 h, quenched with water (150 mL) and extracted with diethyl ether (3 x 100 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, and the solvent removed under vacuum. Chromatography on silica using pentane/dichloromethane as eluent gave a mixture of *E* and *Z* isomers, **17** and **18**, respectively, (6.58 g, 22.2 mmol; 86%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8 Hz, 2H, phenyl *o*-H), 7.29 (m, 3H, phenyl *m*/*p*-H), 5.23 (m, 1H, H_6), 5.11 (m, 1H, H_{10}), 2.40 (m, 1H, H_4), 2.27 (m, 1H, $H_{4'}$), 2.10 (m, 2H, $H_{9,9'}$), 2.02 (t, *J* = 7.5 Hz, 2H, $H_{8,8'}$), 1.81 (m, 2H, $H_{5,5'}$), 1.71 (m, 3H, Me), 1.68 (m, 3H, Me), 1.62 (s, 3H, Me), 1.60 (s, 3H, Me). ^{13}C data for **17**: (100 MHz, $CDCl_3$) δ 136.0 (C_7), 131.7 (C_{11}), 131.5, 128.3, 128.2 (phenyl-*o,m,p*), 124.3 (C_{10}), 123.9 (C_6), 92.9 (C_2), 83.6 (C_1), 68.9 (C_3), 43.6 (C_4), 39.8 (C_8), 30.0 (Me_{15}), 26.7 (C_9), 25.7 (Me_{13}), 23.8 (C_5), 17.8 (Me_{12}), 16.1 (Me_{14}). ^{13}C data for **18**: (100 MHz, $CDCl_3$) δ 136.1 (C_7), 131.7 (C_{11}), 131.6, 128.3, 128.2 (phenyl-*o,m,p*), 124.4 (C_{10}), 122.9 (C_6), 92.9 (C_2), 83.6 (C_1), 68.8 (C_3), 43.9 (C_4), 32.1 (C_8), 30.0 (Me_{15}), 26.7 (C_9), 23.7 (C_5), 23.4 (Me_{13}), 17.7 (Me_{12}), 16.1 (Me_{14}).

*[(E)- and (Z)-1-Phenyl-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol]hexacarbonyl-dicobalt, (**19**) and (**20**).* To a solution of dicobalt octacarbonyl (380 mg, 1.11 mmol) in THF (20 mL) was added a solution of the dienynes **17** and **18** (328 mg, 1.11 mmol) via cannula. Upon stirring for 12 h at room temperature, the deep red solution was concentrated under vacuum and chromatographed on silica using pentane/dichloromethane as eluent to give a mixture of the isomers **19** and **20** as a maroon solid (444 mg, 0,76 mmol; 69%). Further

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separation of the isomers using ethyl acetate/ pentane furnished a pure sample of **19**. Data for **19**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7 Hz, 2H, phenyl *o*-H), 7.36 (t, *J* = 7 Hz, 2H, phenyl *m*-H), 7.31 (t, *J* = 7 Hz, 1H, phenyl *p*-H), 5.16 (t, *J* = 7 Hz, 1H, H_6), 5.08 (t, *J* = 7 Hz, 1H, H_{10}), 2.24 (m, 2H, H_4), 2.16 (m, 2H, H_5), 1.92 (s, 3H, Me_{15}), 1.86 (m, 2H, H_9), 1.79 (m, 2H, H_8), 1.59 (s, 3H, Me_{13}), 1.41 (s, 3H, Me_{14}), 1.40 (s, 3H, Me_{12}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8 (CO's), 136.4 (C_7), 131.7 (C_{11}), 130.0 (phenyl *o*-C), 128.9 (phenyl *m*-C), 127.8 (phenyl *p*-C), 124.3 (C_{10}), 123.7 (C_6), 107.9 (*C*≡CH), 92.4 (C≡*C*H), 75.5 (C-OH), 44.6 (C_4), 39.8 (C_8), 29.7 (Me_{15}), 26.7 (C_9), 25.7 (Me_{13}), 23.4 (C_5), 17.8 (Me_{12}), 16.6 (Me_{14}). IR (CH_2Cl_2) ν(CO) 2087 2050, 2020 cm^{-1}. (MS ESI): $[M - CO]^+$ calcd for $C_{26}H_{28}O_6Co_2$ 554.0550, found 554.0547.

*(E)-3,7-Dimethyl-2,6-octadienyl 2,2,2-trichloroacetate (**22**).* To a solution of geraniol (0.95 mL, 4.50 mmol) in THF (50 mL) at 0 ºC was added sodium hydride (130 mg, 5.4 mmol) and the reaction mixture was stirred for 30 min. It was allowed to warm to room temperature, 2,2,2-trichloroacetyl chloride (0.65 mL, 5.82 mmol) was added and the mixture was stirred overnight at room temperature. After quenching with water (20 mL) and extraction with diethyl ether (2 x 30 mL), the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and evaporated to give a residue that was subjected to flash chromatography on silica to furnish the trichloromethyl ester, **22**, 876 mg, 2.91 mmol; 64%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.41 (t, *J* = 8 Hz, 1H, H_2), 5.05 (t, *J* = 7 Hz, 1H, H_6), 4.84 (d, *J* = 8 Hz, 2H, $H_{1,1'}$), 2.08 (m, 4H, $H_{4,4',5,5'}$), 1.75 (s, 3H, Me_{10}), 1.65 (s, 3H, Me_8), 1.58 (s, 3H, Me_9). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (C=O), 145.4 (C_3), 131.5 (C_7), 123.4 (C_2), 116.2 (C_6), 90.1 (CCl_3), 66.0 (C_1), 39.5 (C_4), 26.1 (C_5), 25.6 (Me_9), 17.6 (Me_8), 16.6 (Me_{10}).

*(E)-3,7-Dimethyl-2,6-octadienyl nonacarbonyltricobaltcarbynylcarboxylate (**23**).(Method A)* To a solution of dicobalt octacarbonyl 960 mg, 2.80 mmol) in THF (20 mL) was added a

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solution of **22** (460 mg, 1.54 mmol) in THF (10 mL) via cannula. After stirring at room temperature for 24 h, the deep red solution was concentrated under vacuum to give a maroon oil that was chromatographed on silica using chloroform/cyclohexane as eluent. The tricobalt ester, **23**, (400 mg, 0.64 mmol; 42%) was isolated as a maroon oil.

*(2E)-3,7-Dimethyl-2,6-octadienyl nonacarbonyltricobaltcarbynylcarboxylate (**23**). (Method B)* To a solution of ethyl nonacarbonyltricobaltcarbynylcarboxylate[26] (0.18 g, 0.35 mmol) dissolved in acetic anhydride (4 mL) was added dropwise a 60% aqueous solution of HPF_6 (0.2 mL, 1.36 mmol). After 30 min, precipitation of a black solid was completed by addition of ether (20 mL) and the solvent was then removed by filtration under a nitrogen atmosphere. The residue was washed three times with ether and finally suspended in CH_2Cl_2 (20 mL). To this was added quickly geraniol (0.5 mL, 2.64 mmol) in CH_2Cl_2 (20 mL) and resulted in formation of a homogeneous purple solution. After removal of solvent, the product was chromatographed on silica using ether/pentane (1:9) as eluent to give the ester **23** (0.20 g, 0.32 mmol; 92%) as a dark purple oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.37 (t, ^3J = 6.5 Hz, 1H, H_2), 5.01 (m, 1H, H_6), 4.71 (d, J = 6.5 Hz, 2H, $H_{1,1'}$), 2.03-1.94 (m, 4H, $H_{4,4',5,5'}$), 1.66 (s, 3H, Me_7), 1.58 (s, 3H, Me_9), 1.51 (s, 3H, Me_{10}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9 (CO's), 178.3 (C=O), 142.9 (C_3), 131.6 (C_7), 123.7 (C_2), 118.2 (C_6), 62.5 (C_1), 39.4 (C_4), 26.3 (C_5), 25.3 (Me_9), 17.3 (Me_8), 16.1 (Me_{10}). IR (CH_2Cl_2) ν(CO) 2105 (m), 2063 (vs), 2045 (s), 1681 (w) cm^{-1}. (MS ESI): $[M - CO]^+$ calcd for $C_{20}H_{17}O_{10}Co_3$ 593.8818, found 593.8822.

(2*E*,6*E*)*-3,7,11-Trimethyl-2,6,10-dodecatrienyl nonacarbonyltricobaltcarbynylcarboxylate (**25**).* As for **23**, ethyl nonacarbonyltricobaltcarbynylcarboxylate (0.28 g, 0.54 mmol) dissolved in acetic anhydride (4 mL), treated with a 60% aqueous solution of HPF_6 (0.3 mL, 2.04 mmol), and subsequently with farnesol (0.3 mL, 1.20 mmol) in CH_2Cl_2 (20 mL) gave, after chromatography on silica using ether/pentane (1:9) as eluent gave the ester **25** as a dark

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purple oil (0.28 g, 0.40 mmol; 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48 (m, 1H, H_2), 5.10 (m, 2H, H_6,H_{10}), 4.82-4.69 (m, 2H, $H_{1,1'}$), 2.06-1.97 (m, 8H, $H_{4,4'}$,$H_{5,5'}$,$H_{8,8'}$,$H_{9,9'}$), 1.77 (s, 3H, Me), 1.68 (s, 3H, Me), 1.60 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6 (CO's), 178.6 (C=O), 143.1, 135.4, 131.1 (C_3, C_7, C_{11}), 124.4, 124.2, 123.6 (C_2, C_6, C_{10}), 62.6 (C_1), 45.0, 44.9 (C_4, C_8), 31.2, 26.8 (Me), 25.7 (Me_{12}), 17.6 (Me_{13}), 16.0, 15.9 (Me_{14},Me_{15}). IR (CH_2Cl_2) ν(CO) 2109 (s), 2065 (s), 2046 (s), 1672 (m) cm^{-1}. (MS ESI): $[M - CO]^+$ calcd for $C_{25}H_{25}O_{10}Co_3$ 661.9443, found 661.9446.

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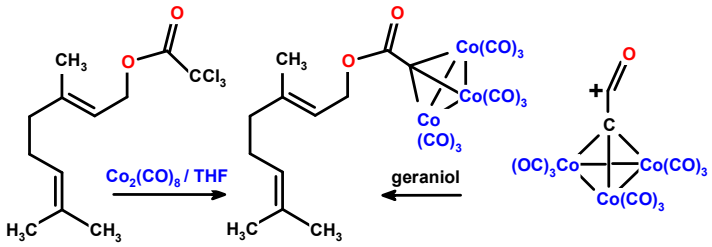

Di- and tri-cobalt carbonyl clusters bearing geranyl or neryl substituents offer potential routes to novel terpenoid systems.