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Abstract: Butyne-1,4-diether hexacarbonyldicobalt complexes (**1**) undergo Lewis acid mediated 4+3 cycloadditions with allylsilanes, incorporating halide from the Lewis acid to give halocycloheptynes (**4**, **6**, **7**). A phenyl group may be incorporated in place of the halogen (to give **8**) by use of benzene as solvent and with $B(C_6F_5)_3$ as the Lewis acid; chlorobenzene and toluene also participate in the process.

Key words: alkyne complexes, cobalt, ring closure, Lewis acids, nucleophiles

The wide occurrence of cycloheptane containing molecules in nature and the limited number of routes of rapid access to seven membered ring systems have sparked much interest in methods for the direct construction of cycloheptanes.[1] As a result of this interest, several research groups have made contributions to the development of cycloaddition reactions for the synthesis of cycloheptanes and their unsaturated counterparts.[2,3] The most widely encountered of these have been 4+3 cycloaddition reactions, particularly versions involving reactions of substituted allyl- or oxyallyl cations with dienes,[4] or those between bis(trimethylsilyl)enol ethers with 1,4-diones.[5]

Suggested location for Scheme 1

We have had an ongoing interest in cycloheptyne hexacarbonyldicobalt complexes, due the availability of reliable methods for substitution of cobalt alkyne complexes,[6] their potential for entering into synthetically useful cycloaddition reactions,[7] and in view of the instability of metal free cycloheptynes.[8,9] Methods of preparation of these cycloheptyne complexes have most often been based on propargyl hexacarbonyldicobalt cation attack by allylsilanes,[10,11] although a ring closing reaction on a propargyl cation by an unactivated alkene[12] and a ring closing metathesis approach also exist.[13,14,15] We have reported a 4+3 cycloaddition route to such

compounds based on the reaction of propargyl cations, formed sequentially by action of BF_3-OEt_2 on **1**, with allyldimetal equivalents **2**.[11] In addition to the cycloheptenyne complexes **3** obtained from this process, under some conditions we obtained fluorocycloheptyne complexes **4**. The presence of **4** suggests that the propargyl cation complex is capable of cyclization onto an alkene function, to at least an equilibrium extent, giving a cycloheptyne complex bearing 2^o alkyl cation which can be trapped by a fluoride source (Scheme 2). This in turn implies that more readily available allylsilanes could be used to obtain compounds such as **4**, and that other nucleophilic species could be incorporated into the cycloheptane complex. As a result we have investigated the feasibility of these Lewis acid mediated 4+3 cycloaddition/nucleophilic trapping reactions between 1,4-butyne-diether-$Co_2(CO)_6$ complexes (**1**) and allyltrimethylsilane. A preliminary account of the results is contained in this report.

Suggested location for structures **1**-**3**

Suggested location for Scheme 2

The 4+3 cycloaddition/trapping process proved to be relatively facile in the presence of BF_3-OEt_2. Slow addition of BF_3-OEt_2 (5 equiv) to a solution of allyltrimethylsilane (1.5 equiv) and **1a** (0.05 M in CH_2Cl_2) afforded **4a** in 60% yield. The main side product from this process proved to be diallylation complex **5a** (21%). Alternative modes of addition were found to give higher yields of **4a**; addition of a BF_3-OEt_2/allyltrimethylsilane mixture to **1a** in CH_2Cl_2 gave 75% of **4a** and 20% of **5a**, while addition of allyltrimethylsilane to a mixture of **1a** and BF_3-OEt_2 gave 75% of **4a** with 8% of **5a**.[16] Use of less than 1.5 equivalents of allyltrimethylsilane gave incomplete conversion, indicative of some destruction of the allylsilane under the reaction conditions. These three sets of conditions were applied to the other cases studied (Table 1), and each approach gave superior results in selected substrate/nucleophile combinations. Other

halogens could be incorporated by replacing BF_3-OEt_2 with alternate Lewis acids. Chlorinative cycloaddition of **1a** could be accomplished by use of $SnCl_4$, giving **6a** in 78% yield. The corresponding bromination product, **7a**, could be obtained with $SnBr_4$, but only in low yield (26%). Other bromide containing Lewis acids, such as BBr_3 and $AlBr_3$, gave no **7a** but extensive decomposition of the cobalt complex.

Suggested location of structures **4-10**

While investigating conditions of optimal fluorination, the reaction of **1a** with BF_3-OEt_2 and allyltrimethylsilane was attempted in benzene as solvent. In addition to a small amount (21%) of fluorination product **4a**, a substantial amount of the tandem 4+3 cycloaddition/Friedel-Crafts alkylation product **8a** (48%) was obtained. Several Lewis acids (Bu_2BOTf, TMSOTf, Et_3B, $B(OAc)_3$, Me_3Al, MAO) were screened for their ability to allow arylation more cleanly. By far the superior Lewis acid for this purpose was found to be $B(C_6F_5)_3$, which afforded **8a** in 70% yield. This process could be extended to other arenes within a narrow nucleophilicity range;[17] toluene as solvent gave **9a** in 58% as an inseparable regioisomeric mixture, while chlorobenzene as solvent gave **10a** (51%) as regioisomeric mixture (from which isomerically pure *ortho*- **10a** could be obtained after repeated chromatography).

Methyl- and phenyl- substituted dicobalt diether complexes **1b** and **1c** were also investigated. Fluorination, chlorination and benzene trapping reactions were readily accomplished on methyl substituted **1b**, giving separable diastereomeric mixtures of the fluorination (**4b**, 74%, *trans*-:*cis*- = 1.6:1) and chlorination products (**6b,** 76%, *trans*-:*cis*- = 1:1.9), but only the *cis*- diastereomer of the phenylation product (**8b**). The stereochemical assignments were made on the basis of the ^{1}H NMR spectra, which suggest that the conformation of these cycloheptyne complexes is well approximated by a cyclohexane- like chair, with the

largest substituent preferring an equatorial orientation. The phenyl substituted substrate **1c** was clearly less reactive to the final cyclization step; although fluorination (**4c**, 67%, *trans*-:*cis*- = 1.5:1) and chlorination (**6c**, 60%, *trans*-:*cis*- = 1:1.9) occurred in reasonable yield, arylation occurred with poor efficiency (***cis*-8c**, 26%) The yield of ***cis*-8c** could be increased to 52% by the addition of CH_2Cl_2 (final volume, 1:4 CH_2Cl_2:benzene) after the addition of the Lewis acid.[18]

Suggested location for Table 1

Reaction of propargyldicobalt cations with unactivated alkenes is infrequent, but precedented.[12,19,20] The resultant cationic intermediates most often eliminate, but they have been trapped by internally located nucleophiles, and halogenation has been observed in cases involving a tertiary cation and benzopyran formation.[20a] Related alkene trapping/fluorination reactions have also been observed in the case of dienyl tricarbonyliron cation initiated cyclohexane-forming reactions. [21] To the best of our knowledge, trapping of these resulting alkyl cations with external carbon nucleophiles has not been reported previously, although Prof. Tyrrell's group has isolated products of further cyclization onto the alkyne unit following an oxidative workup.[20b]

In summary, the ability to use the unactivated alkene in the ring closing step in the 4+3 cycloaddition process allows the use of the less expensive and more readily accessible allylsilanes (relative to the silylstannanes (**2**)). In addition, the ability to trap the resultant cations to give the synthetically useful chloride function, and to arylate the cycloheptynes increases the synthetic flexibility of these 4+3 cycloaddition reactions. Work on expanding this process to incorporate other nucleophiles, and use of the products in further cycloaddition chemistry, are in progress.

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(16) **Typical Experimental Procedure**: To a solution of **1a** (0.065 g) and BF_3-OEt_2 (0.108 g, 5 equiv) in CH_2Cl_2 (6 mL) was added a solution of allyltrimethylsilane (0.026 g, 1.5 equiv) in CH_2Cl_2 (1 mL) over a period of 2 h. Following stirring of the resulting solution for 4h, $NaHCO_{3(aq)}$ was added and the mixture subjected to a conventional extractive workup. Flash chromatographic purification (100% petroleum ether) of the resulting residue afforded sequentially diallylation product **1a** (0.005 g, 8%) and **4a** (0.045 g, 75%).

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(18) **(4a):** IR (neat, NaCl) ν_{max} 2090, 2045, 2015 cm^{-1}; ^1H NMR (0 ^oC) δ 4.76 (dt, J = 44.1_{HF}, 9.2, 1H), 3.14 (m, 2H), 2.85 (m, 2H), 2.0 -2.2 (m, 4H) ; ^{13}C NMR 199.8 (br), 99.1, 94.0 (J_{CF} = 170.2), 35.4 (J_{CF} = 22.6), 28.7 (J_{CF} = 12.2); ^{19}F -92.9 (br m). MS *m/e* 398 (M^+), 370 (M^+-1CO), 342 (M^+-2CO), 314 (M^+-3CO), 286 (M^+-4CO), 258 (M^+-5CO), 230 (M^+-6CO); HRMS *m/e* for $C_{13}H_9Co_2FO_6$ calcd (M^+) 397.9047, found 397.9052. **(*trans*-4b):** IR (neat, NaCl) ν_{max} 2090, 2045, 2019 cm^{-1}; ^1H NMR δ 5.10 (dt, J = 44.3_{HF}, 7.2, 1H), 3.25 (m, 1H), 3.15 (ddd, J = 16.6, 12.0, 4.1, 1H), 3.01 (apparent ddt, J = 16.3, 1.4, 4.1, 1H), 2.35 (m, J = 2H), 1.71 (dddd, J = 37.6_{HF}, 14.6, 12.3, 4.2, 1H), 1.50 (ddd, J = 38.4_{HF}, 14.6, 11.3, 1H), 1.33 (d, J = 6.9, 3H); ^{13}C NMR 200.1 (br), 107.1, 98.8, 89.9 (J_{CF} = 173.0), 41.6 (J_{CF} = 21.6), 33.2 (J_{CF} = 22.0), 31.6 (J_{CF} = 6.3), 27.8 (J_{CF} = 7.0), 21.9; ^{19}F -116.4 (apparent q, J = 38.6); MS *m/e* 412 (M^+), 384 (M^+ - 1CO), 356 (M^+-2CO), 328

(M^+-3CO), 300 (M^+-4CO), 272 (M^+-5CO), 244 (M^+-6CO); HRMS *m/e* for $C_{14}H_{11}Co_2FO_6$ calcd (M^+) 411.9204, found 411.9209. **(*cis*-4b):** IR (neat, NaCl) ν_{max} 2090, 2046, 2014 cm^{-1}; ^1H NMR δ 4.55 (dt, J = 44.0_{HF}, 10.9, 1H), 3.20 (dq, J = 16.6, 3.8, 1H), 2.89 (m, 1H), 2.82 (ddd, J = 16.4, 13.1, 4.4, 1H), 2.3-2.5 (m, 2H), 1.85 (m, 1H), 1.65 (dd, J = 23.8_{HF}, 12.1, 1H), 1.38 (d, J = 6.8, 3H); ^{13}C NMR 200.0 (br), 105.7, 97.3, 95.2 (J_{CF} = 166.9), 45.0 (J_{CF} = 21.8), 36.5, (J_{CF} = 23.1), 34.0 (J_{CF} = 14.4), 30.0 (J_{CF} = 15.3), 22.2; ^{19}F -75.4 (apparent dt, J = 44.0, 21.8); MS *m/e* 412 (M^+), 384 (M^+ - 1CO), 356 (M^+-2CO), 328 (M^+-3CO), 300 (M^+-4CO), 272 (M^+-5CO), 244 (M^+-6CO); HRMS *m/e* for $C_{14}H_{11}Co_2FO_6$ calcd (M^+) 411.9204, found 411.9194. **(*trans*-4c):** IR (neat, NaCl) ν_{max} 2090, 2047, 2026 cm^{-1}; ^1H NMR δ 7.38 (m, 2H), 7.28 - 7.36 (m, 3H), 5.30 (dt, J = 44.4_{HF}, 6.9, 1H), 4.35 (dd, J = 12.5, 3.6, 1H), 3.23 (ddd, J = 16.4, 12.8, 4.1, 1H), 3.11 (d, J = 16.4, 1H), 2.61 (m, 1H), 2.52 (m, 1H), 2.11 (apparent dt, J = 37.9_{HF}, 13.5, 1H), 1.81 (apparent ddt, J = 39.2_{HF}, 4.2, 13.8, 1H) ; ^{13}C NMR 199.6 (br), 142.8, 128.5, 127.5, 127.1, 107.3, 99.9, 90.2 (J_{CF} = 174.8), 42.0 (J_{CF} = 5.7), 38.5 (J_{CF} = 21.4), 33.2 (J_{CF} = 22.3), 27.7 (J_{CF} = 6.5); ^{19}F -119.5 (apparent q, J = 38.1); MS *m/e* 446 (M^+ - 1CO), 418 (M^+-2CO), 390 (M^+-3CO), 362 (M^+-4CO), 334 (M^+-5CO), 306 (M^+-6CO); HRMS *m/e* for $C_{19}H_{13}Co_2FO_6$ calcd (M^+) 445.9411, found 445.9423. **(*cis*-4c):** IR (neat, NaCl) ν_{max} 2091, 2048, 2028 cm^{-1}; ^1H NMR δ 7.38 (m, 2H), 7.2 - 7.3 (m, 3H), 4.71 (dt, J_{HF} = 44.1, 10.8, 1H), 3.97 (d, J = 12.0, 1H), 3.27 (ddd, J = 16.9, 7.5, 3.7, 1H), 2.89 (apparent dt, J = 3.8, 14.7, 1H), 2.60 (dd, J = 21.8, 13.1, 1H), 2.49 (m, 1H), 2.32 (apparent dt, J = 10.8, 12.5, 1H), 2.01 (apparent ddt, J = 10.8, 3.3, 13.1, 1H); ^{13}C NMR 199.5 (br), 142.7, 128.6, 127.3, 127.2, 106.0, 98.1, 95.4 (J_{CF} = 167.5), 44.5 (J_{CF} = 14.7), 41.7 (J_{CF} = 23.1), 36.7 (J_{CF} = 23.0), 30.0 (J_{CF} = 15.1); ^{19}F -75.2 (apparent dt, J = 44.1, 20.6); MS *m/e* 446 (M^+ -

1CO), 418 (M^+-2CO), 390 (M^+-3CO), 362 (M^+-4CO), 334 (M^+-5CO), 306 (M^+-6CO); HRMS *m/e* for $C_{19}H_{13}Co_2FO_6$ calcd (M^+) 445.9411, found 445.9403. **(6a)** IR (neat, KBr) ν_{max} 2088, 2044, 2018, 1991 cm^{-1}; ^1H NMR δ 4.58 (t, J = 7.3, 1H), 3.26 (ddd, J = 16.6, 10.6, 4.1, 2H), 3.03 (apparent dt, J = 16.6, 4.4, 2H), 2.27 (m, 2H), 2.07 (m, 2H); ^{13}C NMR δ 198.8 (br), 99.0, 62.1, 37.1, 30.0; MS *m/e* 414 (M^+), 386 (M^+-1CO), 358 (M^+-2CO), 330 (M^+-3CO), 302 (M^+-4CO), 274 (M^+-5CO), 246 (M^+-6CO); HRMS *m/e* for $C_{13}H_9ClCo_2O_6$ calcd (M^+) 413.8752, found 413.8755. **(*trans*-6b):** IR (neat, KBr) ν_{max} 2090, 2045, 2017 cm^{-1}; ^1H NMR δ 4.67 (t, J = 6.4, 1H), 3.40 (m, 1H), 3.33 (ddd, J = 16.6, 12.4, 4.2, 1H), 3.08 (apparent dt, J = 16.6, 3.4, 1H), 2.25-2.35 (m, 2H), 1.93 (m, 1H), 1.68 (dd, J = 14.4, 1.3, 1H), 1.33 (d, J = 6.8, 3H); ^{13}C NMR δ 200.2 (br), 106.4, 98.1, 61.3, 44.1, 35.8, 33.2, 29.4, 21.6; MS *m/e* 428 (M^+), 400 (M^+-1CO), 372 (M^+-2CO), 344 (M^+-3CO), 316 (M^+-4CO), 288 (M^+-5CO), 260 (M^+-6CO); HRMS *m/e* for $C_{14}H_{11}ClCo_2O_6$ calcd (M^+-2CO) 371.9010, found 371.9006. **(*cis*-6b):** IR (neat, KBr) ν_{max} 2090, 2046, 2015 cm^{-1}; ^1H NMR δ 3.99 (tt, J = 11.1, 1.7, 1H), 3.22 (dt, J = 16.6, 3.4, 1H), 2.94 (m, 1H), 2.87 (ddd, J = 16.6, 12.7, 4.0, 1H), 2.52 (m, 1H), 2.48 (m, 1H), 1.99 (m, 1H), 1.79 (m, 1H), 1.35 (d, J = 6.7, 3H); ^{13}C NMR δ 200.1 (br), 105.5, 97.0, 61.8, 49.0, 40.4, 36.9, 32.8, 22.0; MS *m/e* 428 (M^+), 372 (M^+-2CO), 344 (M^+-3CO), 316 (M^+-4CO), 288 (M^+-5CO), 260 (M^+-6CO); HRMS *m/e* for $C_{14}H_{11}ClCo_2O_6$ calcd (M^+-2CO) 371.9010, found 371.9006. **(*trans*-6c):** IR (neat, NaCl) ν_{max} 3037, 2090, 2048, 2027 cm^{-1}; ^1H NMR δ 7.37 (t, J = 7.5, 2H), 7.28-7.35 (m, 3H), 4.85 (t, J = 6.3, 1H), 4.52 (dd, J = 12.0, 3.6, 1H), 3.40 (ddd, J = 16.6, 12.5, 4.1, 1H), 3.15 (dt, J = 16.6, 3.3, 1H), 2.52 (m, 1H), 2.42 (m, 1H), 2.36 (apparent t, J = 13.5, 1H), 2.08 (m, 1H); ^{13}C NMR δ 199.9 (br), 142.7, 128.5, 127.6, 127.2, 106.6, 99.1, 61.4, 43.9, 40.9, 36.0, 29.5; MS *m/e* 462 (M^+-

CO), 434 (M^+-2CO), 406 (M^+-3CO), 378 (M^+-4CO),350 (M^+-5CO), 322 (M^+-6CO); HRMS *m/e* for $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9162. **(*cis*-6c:)** IR (neat, NaCl) ν_{max} 3030, 2092, 2048, 2028, 2016 cm^{-1}; ^1H NMR δ 7.37 (t, J = 7.4, 2H), 7.25-7.35 (m, 3H), 4.14 (tt, J = 11.0, 1.8, 1H), 4.00 (dd, J = 12.2, 3.5, 1H), 3.29 (tt, J = 16.8, 3.4, 1H), 2.95 (ddd, J = 16.8, 12.7, 4.1, 1H), 2.74 (m, 1H), 2.63 (m, 1H), 2.45 (m, 1H), 2.15 (m, 1H); ^{13}C NMR δ 199.5 (br), 142.6, 128.6, 127.3, 127.2, 105.7, 98.0, 62.0, 47.5, 45.8, 40.7, 32.9; MS *m/e* 462 (M^+-1CO), 434 (M^+-2CO), 406 (M^+-3CO), 378 (M^+-4CO), 350 (M^+-5CO), 322 (M^+-6CO); HRMS *m/e* for $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9164. **(7a):** IR (neat, KBr) ν_{max} 2090, 2046, 2016 cm^{-1}; ^1H NMR δ 4.75 (t, J = 6.9, 1H), 3.27 (ddd, J = 16.7, 10.7, 3.7, 2H), 3.09 (dt, J = 16.7, 3.7, 2H), 2.33 (m, 2H), 2.07 (m, 2H); ^{13}C NMR δ 200.0 (br), 98.8, 56.6, 37.5, 31.5; MS *m/e* 458 (M^+), 402 (M^+-2CO), 374 (M^+-3CO), 348 (M^+-4CO), 318 (M^+-5CO), 290 (M^+-6CO); HRMS *m/e* for $C_{13}H_9Br^{79}Co_2O_6$ calcd (M^+) 457.8246, found 457.8242. **(8a):** IR (neat, KBr) ν_{max} 3028, 2087, 2043, 2013 cm^{-1}; ^1H NMR δ 7.31 (t, J = 7.4, 2H), 7.21 (t, J = 7.5, 1H), 7.17 (d, J = 7.6, 2H), 3.29 (dt, J = 16.5, 3.2, 2H), 2.91 (ddd, J = 16.5, 12.5, 4.1, 2H), 2.59 (t, J = 10.6, 1H), 2.14 (dt, J = 13.9, 3.4, 2H), 1.88 (m, 2H); ^{13}C NMR δ 200.0 (br), 149.5, 128.7, 126.3, 126.0, 100.4, 49.3, 38.1, 34.7; MS *m/e* 456 (M^+), 400 (M^+-2CO), 372 (M^+-3CO), 344 (M^+-4CO), 316 (M^+-5CO), 288 (M^+-6CO); HRMS *m/e* for $C_{19}H_{14}Co_2O_6$ calcd (M^+-2CO) 371.9607, found 371.9604. **(*cis*-8b):** IR (neat, KBr) ν_{max} 3030, 2088, 2044, 2021 cm^{-1}; ^1H NMR δ 7.31 (m, 2H), 7.20 (m, 1H), 7.15 (d, J = 7.1, 2H), 3.29 (dt, J = 16.4, 3.1, 1H), 3.03 (m, 1H), 2.95 (ddd, J = 16.6, 12.6, 4.0, 1H), 2.66 (t, J = 10.7, 1H), 2.10 (dt, J = 14.1, 3.6, 1H), 2.03 (dd, J = 14.0, 3.9, 1H), 1.86 (m, 1H), 1.65 (m, 1H), 1.33 (d, J = 6.8, 3H); ^{13}C NMR δ 200.4 (br), 149.6, 128.7, 126.2, 126.0, 107.4, 99.1, 48.4,

46.6, 39.1, 37.8, 35.0, 22.3; MS *m/e e* 434 (M^+), 414 (M^+-2CO), 386 (M^+-3CO), 358 (M^+-4CO), 330 (M^+-5CO), 302 (M^+-6CO); HRMS *m/e* for $C_{20}H_{16}Co_2O_6$ calcd (M^+-3CO) 385.9763, found 385.9766. **(*cis*-8c):** IR (neat, KBr) ν_{max} 3029, 2089, 2045, 2026, 2008 cm^{-1}; ^1H NMR δ 7.18-7.37 (m, 10H), 4.11 (m, 1H, simplifies to dd, J = 9.7, 5.6 upon irradiation at δ 2.83), 3.37 (dt, J = 16.4, 3.2, 1H), 3.03 (ddd, J = 16.4, 12.6, 4.1, 1H), 2.83 (br t, J = 10.7, 1H), 2.28-2.37 (m, 2H), 2.22 (dt, J = 14.1, 3.1, 1H), 2.04 (m, 1H); ^{13}C NMR δ 199.9 (br), 149.3, 143.7,128.7, 128.4, 127.3, 127.0, 126.3, 126.1, 107.4, 100.3, 50.0, 48.9, 43.5, 37.9, 35.1; MS *m/e* 504 (M^+-1CO), 448 M^+-3CO), 420 (M^+-4CO), 392 (M^+-5CO), 364 (M^+-6CO); HRMS *m/e* for $C_{25}H_{18}Co_2O_6$ calcd (M^+-3CO) 447.9920, found 447.9917. **(9a):** (1.4:1:1 *ortho:para:meta* mixture) IR (neat, KBr) ν_{max} 3022, 2088, 2043, 2017 cm^{-1}; ^1H NMR δ 6.92-7.22 (m, 4H), 3.29 (m, 2H), 2.90 (m, 2H), 2.80 (t, J = 10.2), 2.56 (t, J = 10.6) and 2.55 (t, J = 10.6) (1H), 2.35 (s), 2.34 (s), and 2.33 (s) (3H), 2.11 (m, 2H), 1.86 (m, 2H); ^{13}C NMR δ 200.7 (br), 200.0 (br), 149.5, 147.6, 146.6, 138.3, 135.5, 133.7, 130.4, 129.3, 128.6, 127.1, 126.8, 126.4, 126.2, 125.7, 123.3, 100.4, 100.2, 49.3, 48.8, 38.3, 38.2, 37.7, 35.1, 34.8, 34.7; MS *m/e* 470 (M^+), 414 (M^+-2CO), 386 (M^+-3CO), 358 (M^+-4CO), 330 (M^+-5CO), 302 (M^+-6CO); HRMS *m/e* for $C_{20}H_{16}Co_2O_6$ calcd (M^+ -3CO) 385.9763, found 385.9767. **(10a):** (1.8:1:0.3 *ortho:para:meta* mixture) (***ortho*-10a**): IR (neat, KBr) ν_{max} 2096, 2048, 2030, 2015, 1994 cm^{-1}; ^1H NMR δ 7.38 (dd, J = 8.0, 1H), 7.19-7.27 (m, 2H), 7.14 (m, 1H), 3.30 (dt, J = 16.4, 3.1, 2H), 3.14 (br, 1H), 2.97 (ddd, J = 16.4, 12.6, 4.2, 2H), 2.13 (dt, J = 13.9, 3.3, 2H), 1.85 (br m, 2H); ^{13}C NMR δ 200.2 (br), 151.0, 146.2, 132.4, 129.6, 127.1, 127.0, 100.3, 44.0, 37.3, 34.8; MS *m/e* 434 (M^+-2CO), 406 (M^+-3CO), 378 (M^+-4CO), 350 (M^+-5CO), 322 (M^+-6CO); HRMS *m/e* for $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9168. Peaks

attributable to the para isomer could be observed at ^{1}H NMR δ 7.28 (d, J = 8.3, 2H), 7.09 (d, J = 8.3, 2H), 3.28 (m, obscured, 2H), 2.90 (ddd, J = 16.5, 12.6, 4.1, 2H), 2.57 (t, J = 10.6, 1H), 2.09 (dt, J = 14.0, 3.4, 2H), 18.3 (m, 2H) ; ^{13}C NMR δ 200.6 (br), 147.8, 131.7, 128.8, 127.6, 100.1, 48.6, 38.1, 34.6. Peaks from the meta isomer could be observed at ^{1}H NMR δ 7.24 (apparent t, J = 7.7, 1H), 7.18 (br d, J = 8.5, 1H), 7.16 (br s, 1H), 7.05 (d, J = 7.5, 1H), 2.12 (m, obscured, 2H); ^{13}C NMR δ 151.3, 134.3, 130.0, 126.6, 126.1, 124.5, 48.9, 38.0.

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