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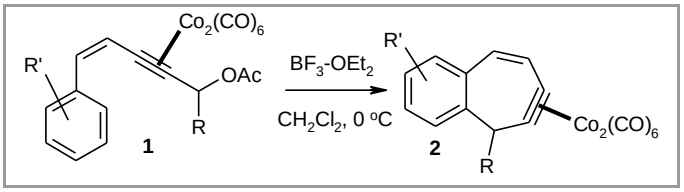
Abstract: Lewis acid mediated intramolecular Nicholas reactions of aryl (*Z*)-enyne propargyl acetate-$Co_2(CO)_6$ complexes **1** afford benzocycloheptenyne-$Co_2(CO)_6$ complexes **2** and their heterocyclic analogues.

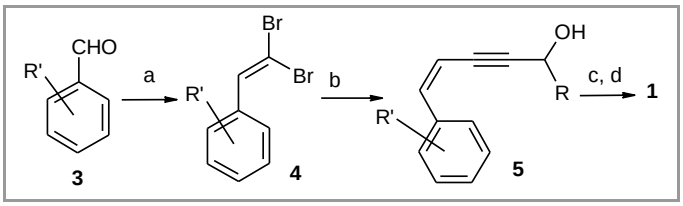
Key words: Nicholas reactions, alkynes, arenes, complexes, transition metals.

The use of acyclic alkynedicobalt complexes and Nicholas reactions[1] have proven themselves to be highly successful in the rapid preparation of cycloheptyne-$Co_2(CO)_6$ complexes.[2-4] Only a limited number of ring fused versions of these cycloheptyne complexes known; of these, our interest has been drawn to the benzocycloheptyne complexes. Just one report of the synthesis of benzocycloheptynedicobalt complexes has been published, involving an impressive carbonylative Heck reaction of an enyne complex.[5] Nevertheless, the success of this process required replacement of two CO ligands by a dppm ligand, and furthermore employed diphenylacetylene-$Co_2(CO)_6$ as the optimal carbonylation source. A variety of naturally occurring compounds containing benzocycloheptane units are known, particularly the icetexanes[6] or other diterpenes[7] and the colchicines,[8] or their heterocyclic analogues, particularly the furanocycloheptanes.[9] Therefore, we considered further synthetic effort towards the ready synthesis of benzocycloheptynedicobalt systems to be of importance. Given the known ability of propargyldicobalt cations to enter in Nicholas reaction with electron rich arenes, it was our belief that the ionization of **1** would provide access to benzocycloheptynedicobalt complexes **2** by way of an intramolecular Nicholas reaction.



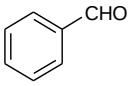
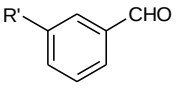
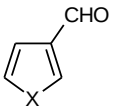
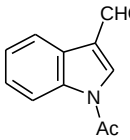
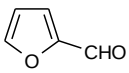
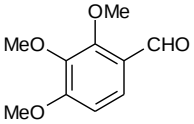
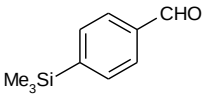
Equation 1 Intramolecular Nicholas reaction for benzocycloheptenyne-$Co_2(CO)_6$ preparation.

The substrates for these cyclization reactions were derived from the appropriate arylaldehydes **3** (Scheme 1). Carbon tetrabromide-PPh_3 mediated conversion of **3** to the corresponding dibromoalkenes (**4**) occurred in high yield.[10] Critical for access of *Z*-alkenes of high stereochemical purity was the stereoselective Pd catalyzed reduction of the *trans* carbon-bromine bond of **4**, with subsequent Sonogashira coupling of the remaining *cis* bromide and the appropriate propargyl alcohol without intermediate isolation, according to the method of Uenishi.[11] The *Z* enyne-propargyl alcohols **5** were obtained in fair to good yields,[12] and were subjected to acetylation and complexation under conventional conditions to afford **1**.[13]



Scheme 1 *Reagents and conditions:* (a) CBr_4, PPh_3, CH_2Cl_2; (b) Bu_3SnH, $Pd(PPh_3)_4$, CH_2Cl_2; then HN^iPr_2, CuI, propargyl alcohol; (c) Ac_2O, pyridine; (d) $Co_2(CO)_8$, CH_2Cl_2.

Table 1 Preparation of propargyl acetate **1**. Yields of intermediates

	ArCHO **3**	Yield **4**(%)	Yield **5**(%)	Yield **1**(%)
a		94	71	80
b R'=Me		92	58	86
c R'=OMe		100	49	76
d R'=OMe R=Me		-	90	70
e R'=OMe R=Ph		-	70	80
f X=O		94	54	70
g X=S		90	51	81
h		77	62	72
i		93	65	70
j		100	45[a]	85[b]
k		91	68	80

[a] Yield of isolated acetate
[b] Yield based on acetate

With the requisite substrates in hand, attention was turned to cyclization reactions. BF_3-OEt_2 was chosen as the preferred Lewis acid due to its minimized tendency to induce decomposition in related cobalt complexes.[14] Although unactivated arenes are generally insufficiently reactive to participate in Nicholas reactions, unsubstituted arene **1a** did undergo gradual reaction at 0 °C. After 3.5 h, a small amount of starting material remained, but benzocycloheptyne **2a** could be isolated in 49% yield (58% yield based on recovered starting material). Longer reaction periods resulted in increased amounts of unproductive decomposition.

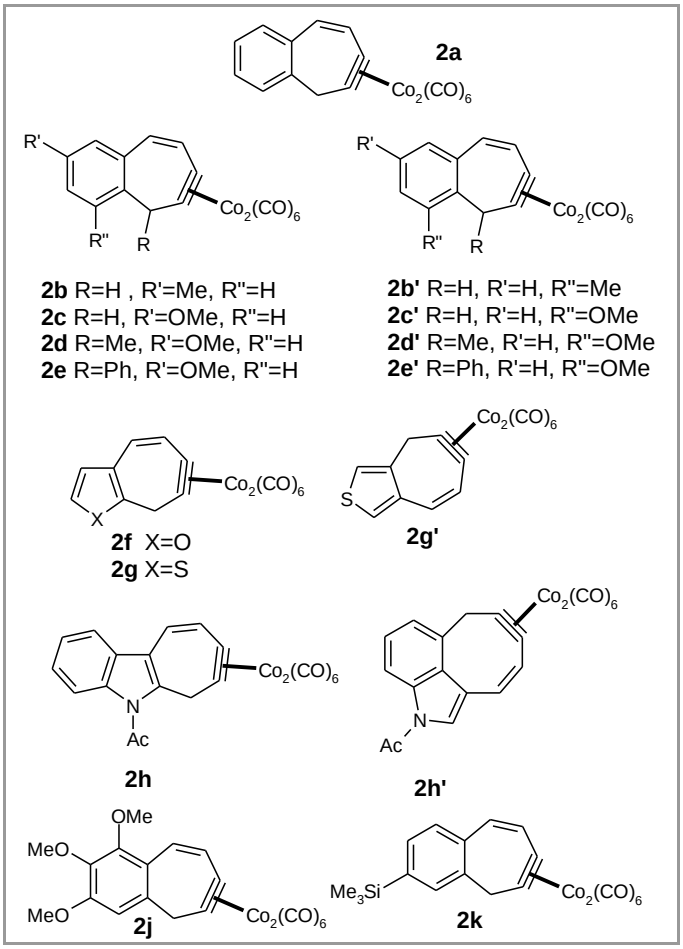


Figure 1 Benzocycloheptenynedicobalt cylization products **2**.

With electron donating substituents on the benzene ring, the reactions were noticeably more rapid. *m*-Methyl substituted **1b** and *m*-methoxy substituted **1c** underwent complete starting material consumption in 1.5 h and 0.5 h, respectively. Compound **2b** was obtained in 67% yield as a mixture of products of substitution *p*- and *o*- to the methyl group (**2b**:**2b'** = 3.5:1, inseparable**)**, whereas methoxy compound **2c** was obtained in 53% yield as a 4.9:1 separable mixture of **2c** and **2c'**. Substitution at the propargylic site did not interfere with the cyclization process. Despite the potential for a competitive elimination process, methyl substituted **1d** reacted readily, giving **2d** in good yield (77%, **2d**:**2d'**=7:1, separable) and with no elimination side-product. Phenyl-substituted **2e** also reacted promptly, affording **2e** in excellent yield (90%, **2e**:**2e'**=12.5:1, separable).

Heteroaryl based systems were also capable of forming the corresponding fused cycloheptyne complexes. 3-Substituted furyl system **1f** afforded **2f** quickly and in good yield (78%). The corresponding thienyl system also cyclized rapidly, but gave a small amount of C-4 substitution product **2g'** in addition to the expected **2g** (83% yield, **2g**:**2g'**=5:1, inseparable).[15] The C-3 substituted indole substrate **1h** gave cycloheptyne complex **2h** in 38% yield, but the major product was actually cyclooctyne complex **2h'** (47% yield), the result of competitive reaction through C-4.

Accomplishing cyclization at sites disfavoured for electrophilic aromatic substitution by the existing substituents or by the ring system itself proved to be more problematic, but possible in some cases. 2-Substituted furyl system **1i** gave only dimeric-oligomeric products under conventional conditions. Higher dilution conditions did result in a product mixture apparently containing a benzocycloheptenyne complex, but it was both in low yield and not readily purified. Trimethoxyarene **1j** also cyclized only in low yield (22%) to give **2j** under conventional conditions, but high dilution conditions (10^{-3}M) allowed formation of **2j** in 51% yield. As a result of these difficulties, our choice of a *p*-disubstituted substrate for investigation was *p*-trimethylsilyl arene **1k**, by virtue of the minimally *o*-/*p*- activating nature of the TMS group and the facility with which arylsilanes are converted into other arenes.[16] In the event, reaction of **1k** was somewhat slow, and it was again prudent to stop the reaction before complete starting material consumption, but **2k** could be obtained in 58% yield (70% based on recovered starting material).[17]

Table 2 Cycloheptenyne complexes **2** from propargyl acetates **1**

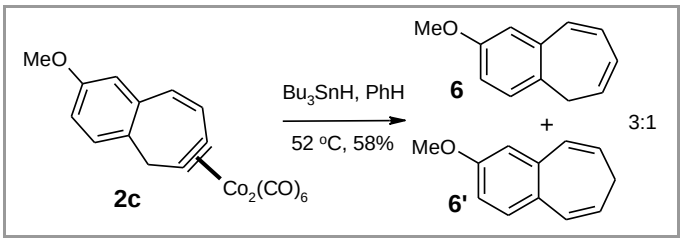
Starting **1**	Reaction time (h)	Product **2**	Yield[a,b]
1a	3.5	**2a**	49 [58]
1b	1.5	**2b/2b'**	67 (3.5:1)
1c	0.5	**2c/2c'**	53 (4.9:1)
1d	0.5	**2d/2d'**	77 (7.0:1)
1e	0.5	**2e/2e'**	90 (12.5:1)
1f	0.5	**2f**	78
1g	0.5	**2g/2g'**	83 (5.0:1)
1h	2	**2h/2h'**	85 (0.81:1)
1j	0.5	**2j**	51[c]
1k	4	**2k**	58 [70]

a) Yields in square brackets are based on recovered starting material
b) Numbers in parentheses are **2:2'** ratios
c) Conducted under high dilution (10^{-3} M) conditions

We wished to demonstrate the possibility of removal of the metal complex in one of these cases. Therefore, substrate **2c** was chosen for reductive decomplexation under the Bu_3SnH protocol of Isobe.[18] Under the literature conditions (Bu_3SnH, benzene, 65 °C) modest yields of a mixture of benzocycloheptadiene **6** were obtained along with its double bond migration isomer **6'** (40% yield,

6:6' = 2:1). Reducing the reaction temperature to 52 °C allowed improvement in both the yield and isomeric ratio (58% yield, **6**:**6'**= 3:1).

In summary, a series of benzocycloheptenynedicobalt complexes may be obtained by intramolecular Nicholas reactions of arenes or their heterocyclic analogues. Both electron neutral and electron rich arenes will participate in the process, although difficulties may be encountered where the existing substitutents direct strongly away from the intended site of intramolecular attack. The hexacarbonyldicobalt unit may be removed with concomitant reduction of the alkyne function. The use of blocking groups to address regiochemical issues, and application of this chemistry to dibenzocycloheptynedicobalt complexes, are under study and will be reported in due course.



Equation 2 Reductive decomplexation of a benzocycloheptenyne complex.

Acknowledgment

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(12) Selected compounds: (**5b**) IR (neat, KBr) υ_{max} 3345, 3020, 2920, 2193 cm^{-1}; ^1H NMR: δ 1.77(1H, br), 2.38(3H, s), 4.50(1H, d, J=2.0), 5.71(1H, dt, J=11.9, 2.0), 6.64 (1H, d, J=11.9), 7.11 (1H, d, J=7.5), 7.27(1H, dd, J=7.7, 7.5), 7.63 (1H, s), 7.68 (1H, d, J=7.7); ^{13}C NMR: δ 139.4, 137.8, 136.1, 129.4, 128.2, 125.6, 106.5, 93.6, 84.3, 51.8, 21.4; MS (EI, m/z) 172; HRMS (EI, m/z) for $C_{12}H_{12}O$ calcd 172.0888, found 172.0888. (**5g**) IR (neat, KBr) υ_{max} 3358, 3097, 2918, 2191, 1699, 1602 cm^{-1}; ^1H NMR: δ 2.39(1H, s), 4.51(2H, d, J=2.0), 5.62(1H, dt, J=11.7, 2.3), 6.70(1H, d, J=11.7), 7.29(1H, dd, J=4.9, 2.55), 7.62(1H, d, J=5.0), 7.76(1H, d, J=2.1); ^{13}C NMR: δ 138.3, 133.0, 127.7, 125.6, 125.2, 105.2, 93.8, 84.4, 51.6; MS (EI, m/z) 164; HRMS (EI, m/z) for C_9H_8OS calcd 164.0296, found 164.0292.

(13) Selected compounds: (**1b**) IR (neat, KBr) υ_{max} 3014, 2927, 2092, 2024, 1748 cm^{-1}; ^1H NMR: δ 2.03 (3H, s), 2.39(3H, s), 4.52(2H, s), 6.61(1H, d, J=11.0), 6.80 (1H, d, J=11.0), 7.02(2H, d, J=8.2), 7.14(1H, d, J=7.6), 7.29(1H, d, J=7.5); ^{13}C NMR: δ 199.1(br), 170.5, 138.2, 137.6, 132.5, 129.0, 128.5, 128.4, 127.5, 125.4, 91.4, 83.5, 64.9, 21.3, 20.3; MS (EI, m/z) 472$[M\text{-}CO]^+$, 444$[M\text{-}2CO]^+$, 416$[M\text{-}3CO]^+$, 388$[M\text{-}4CO]^+$, 360, $[M\text{-}5CO]^+$, 332$[M\text{-}6CO]^+$; HRMS (EI, m/z) for $C_{20}H_{14}Co_2O_8$ calcd 443.9454$[M\text{-}2CO]^+$, found 443.9457. (**1g**) IR (neat, KBr) υ_{max} 3013, 2956, 2092, 2022, 1746 cm^{-1};^1H NMR: δ 2.07(3H, s), 4.73(2H, s), 6.62(1H, d, J=11.0),6.67(1H, d, J=11.0), 6.98(1H, d, J=4.3), 7.13(1H, s). 7.38(1H, s); ^{13}C NMR: δ 199.3(br), 170.5, 138.2, 128.3, 128.2, 126.8, 126.2, 123.4, 91.4, 83.3, 64.5, 20.3; MS (EI, m/z): 464$[M\text{-}CO]^+$, 436$[M\text{-}2CO]^+$, 408$[M\text{-}3CO]^+$, 380$[M\text{-}4CO]^+$, 352$[M\text{-}5CO]^+$, 324$[M\text{-}6CO]^+$; HRMS (EI, m/z) for $C_{17}H_{10}Co_2O_8S$ calcd 435.8862$[M\text{-}2CO]^+$, found: 435.8853.

(14) **Experimental Procedure**: To a stirred ice cold solution of the propargyl acetate complex (0.2 mmol) in CH_2Cl_2 (20 mL), was added $BF_3.OEt_2$ (85.2 mg, 0.60 mmol) in CH_2Cl_2 (4 mL) over 10 minutes. After stirring at 0 °C for the time indicated in Table 2, saturated sodium bicarbonate solution was added, and the mixture was subjected to a conventional workup. Purification by flash chromatography afforded sequentially the benzocycloheptenyne complex and any recovered starting material.

(15) This reflects a tendency for a slightly lower preference for C-2 reactivity in thiophenes relative to furans and perhaps the known tendency for electron withdrawing C-3 groups to deactivate C-2 to a greater degree than C-4; Taylor, R. In *The Chemistry of Heterocyclic Compounds*; Gronowitz, S., Ed.; Wiley: New York, 1986; Vol 44**,** Part 2, Ch.1, p.16.

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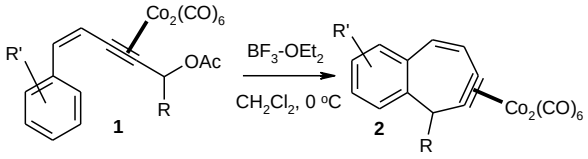
(17) (**2a**) IR (neat, KBr) υ_{max} 2929, 2091, 2021,1574 cm^{-1}; ^1H NMR: δ 4.18 (2H, s), 6.77(1H, d, J=10.1), 6.93(1H, d, J=10.1), 7.22(4H, m); ^{13}C NMR**:** δ 199.3(br), 137.5, 137.3, 133.1, 132.5, 129.4, 128.9, 128.8, 126.9, 102.3, 86.5, 40.8; MS (EI, m/z): 426$[M]^+$, 398$[M\text{-}CO]^+$, 370$[M\text{-}2CO]^+$, 342$[M\text{-}3CO]^+$, 314$[M\text{-}4CO]^+$, 286$[M\text{-}5CO]^+$, 258$[M\text{-}6CO]^+$; HRMS (EI, m/z) for $C_{17}H_8Co_2O_6$ calcd 426.9063$[M+H]^+$, found 426.9069. (**2b**) IR (neat, KBr) υ_{max} 3014, 2858, 2090, 2053, 2021, 1557 cm^{-1}; ^1H NMR: δ 2.31 (3H, s), 4.14(2H, s), 6.72(1H, d, J=10.1), 6.90(1H, d, J=10.1), 7.00(1H, s), 7.07(1H, d, J=7.9), 7.15(1H, d, J=7.6); resonances for minor regioisomer **(2b')** could be

observed at 2.51(3H, s), 4.10(2H, s), 6.82(1H, d, J=10.0), 6.93(1H, d, J=10.0), 7.03(1H, m), 7.10(1H, m), 7.17(1H, m); ^{13}C NMR: δ 199.4(br), 137.3, 136.4, 134.5, 133.2, 129.6, 129.4, 128.5, 102.5, 86.9, 40.4, 20.7; resonances for the minor regioisomer could be observed at 133.8, 130.7, 130.4, 128.8, 126.3, 34.2, 21.1; MS (EI, m/z): 440[M]$^+$, 412[M-CO]$^+$, 384[M-2CO]$^+$, 356[M$^+$-3CO], 328[M-4CO]$^+$, 300[M-5CO]$^+$, 272[M-6CO]$^+$; HRMS (EI, m/z) for $C_{18}H_{10}Co_2O_6$ calcd 439.9141 found 439.9137. (**2c**) IR (neat, KBr) υ_{max} 3014, 2956, 2837, 2090, 2050, 2020, 1604 cm^{-1}; ^{1}H NMR: δ 3.77(3H, s), 4.10(2H, s), 6.68(1H, d, J=10.1), 6.71(1H, s), 6.79(1H, d, J=8.3), 6.92(1H, d, J=10.1), 7.16(1H, d, J=8.3); ^{13}C NMR: δ 199.3(br), 158.3, 138.6, 132.8, 130.5, 130.0, 129.3, 117.7, 113.9, 102.9, 86.6, 55.3, 39.9; MS (EI, m/z): 456[M]$^+$, 428[M-CO]$^+$, 400[M-2CO]$^+$, 372[M-3CO]$^+$, 344[M-4CO]$^+$, 316[M-5CO]$^+$, 288[M-6CO]$^+$; HRMS (EI, m/z) for $C_{18}H_{10}Co_2O_7$ calcd 455.9090**,** found: 455.9051. (**2e**) IR (neat, KBr) υ_{max} 3026, 2935, 2090, 2052, 2022, 1602, 1556 cm^{-1}; ^{1}H NMR: δ 3.88(3H, s), 5.35 (1H, s), 6.77(1H, dd, J=8.6, 2.6), 6.82(1H, s), 6.83(1H, m), 7.01(1H, d, J=10.1), 7.09(1H, d, J=8.5), 7.23(1H, m), 7.29(2H, m), 7.35(2H, m); ^{13}C δ199.4(br), 158.3, 144.4, 138.3, 133.5, 133.1, 131.3, 129.6, 128.6, 127.0, 118.4, 114.2, 107.1, 84.8, 55.4, 55.3; MS (EI, m/z): 504[M-CO]$^+$, 476[M-2CO]$^+$, 448[M-3CO]$^+$, 420[M-4CO]$^+$, 392[M-5CO]$^+$, 364[M-6CO]$^+$; HRMS (EI, m/z) for $C_{24}H_{14}Co_2O_7$ calcd 503.9454[M-CO]$^+$, found 503.9437. (**2f**) IR (neat, KBr) υ_{max} 3025, 2928, 2092, 2051, 2020; ^{1}H NMR: δ 4.47 (2H, s), 6.31(1H, s), 6.39(1H, d, J=9.6), 6.57(1H, d, J=9.6), 7.30(1H, s); ^{13}C NMR: δ 199.3(br), 148.8, 140.8, 125.1, 124.1, 120.5, 113.3, 92.2, 86.6 34.0; MS (EI, m/z): 416[M]$^+$, 388[M-CO]$^+$, 360[M-2CO]$^+$, 332[M-3CO]$^+$, 304[M-4CO]$^+$, 276[M-5CO]$^+$, 248[M-6CO]$^+$; HRMS (EI, m/z) for $C_{15}H_6Co_2O_7$ calcd 415.8777[M]$^+$, found 415.8752. (**2g**) IR (neat, KBr) υ_{max} 2926, 2856, 2092, 2055, 2024, 1699, 1650, 1540 cm^{-1}; ^{1}H NMR: δ 4.45 (2H, s), 6.68 (1H, ½ AB quartet, J=16.0), 6.74 (1H, ½ AB quartet, J=16.1), 6.88(1H, d, J=8.7), 7.08(1H, d, J=8.8); resonances for minor regioisomer **(2g')** could be observed (in CD_3CN) at δ 4.34(2H, s), 6.66(1H, d, J=9.9), 6.80(1H, d, J=9.7), 7.20(1H, s), 7.38(1H, s); ^{13}C NMR**:** δ 199.1(br), 136.8, 136.7, 132.0, 126.4, 126.2, 122.0, 97.6, 86.8, 34.6; resonances for the minor regioisomer could be observed at 128.7, 126.9, 124.8, 35.5; MS (EI, m/z): 432[M]$^+$, 404[M-CO]$^+$, 376[M-2CO]$^+$, 348[M-3CO]$^+$, 320[M-4CO]$^+$, 292[M-5CO]$^+$, 264[M-6CO]$^+$; HRMS (EI, m/z) for $C_{15}H_6Co_2O_6S$ calcd 403.8575 [M-CO]$^+$, found 403.8554. (**2j**) IR (neat, KBr) υ_{max} 3055, 2090, 2051, 2021, 1594 cm^{-1}; ^{1}H NMR: δ 3.78 (s, 3H), 3.83 (3H, s), 3.91 (3H, s), 4.05 (2H, s), 6.62 (1H, s), 6.93 (1H, d, J = 10.4), 7.12 (1H, d, J = 10.4); ^{13}C NMR: δ 199.4, 153.3, 152.8, 141.4, 134.3, 127.7, 125.9, 124.7, 108.4, 102.9, 87.7, 61.1, 61.0, 56.0, 41.1. MS (EI, m/z) 516 [M]$^+$, 460 [M-2CO]$^+$, 404 [M-4CO]$^+$; HRMS for $C_{20}H_{14}Co_2O_9$ calcd 403.9505 [M-4CO]$^+$, found 403.9492. (**2k**) IR (neat, KBr) υ_{max} 3014, 2957, 2360, 2091, 2052, 2022 cm^{-1}; ^{1}H NMR: δ 0.28(9H, s), 4.20 (2H, s), 6.76(1H, d, J=10.1), 6.94(1H, d, J=10.1), 7.16(1H, d, J=7.5) 7.36(1H, s), 7.37(1H, d, J=6.2); ^{13}C NMR: δ 199.4(br), 142.0, 137.7, 136.3, 134.2, 133.2, 131.9, 131.7, 129.0, 102.4, 86.6, 40.9, -1.2; MS (EI, m/z): 498[M]$^+$, 470[M-CO]$^+$, 442[M-2CO]$^+$, 414[M-3CO]$^+$, 386[M-4CO]$^+$, 358[M-5CO]$^+$, 330[M-6CO]$^+$; HRMS (EI, m/z) for $C_{20}H_{16}Co_2O_6Si$ calcd 469.9431[M-CO]$^+$, found 469.9434.

(18) Hosokawa, S.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 2609.

Graphical Abstract



Benzocycloheptynedicobalt Complexes by Intramolecular Nicholas Reactions

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