Cycloheptyne–cobalt complexes *via* allylation of stabilized γ-carbonyl cations

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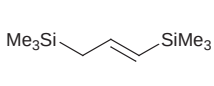
The Bu_2BOTf mediated reaction of stannylsilanes (5 and 9) with γ-methoxy-alkynoate and -alkynone hexacarbonyldicobalt complexes (8), followed by conversion of the organic carbonyl into an acetate and a $BF_3{\cdot}OEt_2$ mediated intramolecular reaction, affords cycloheptenyne hexacarbonyldicobalt complexes (13 and 15).

Cyclic alkynes are compounds of limited stability.[1] The smallest unsubstituted member of the series which can be isolated under conventional laboratory conditions is cyclooctyne; in the vast majority of cycloheptynes and smaller cycloalkynes, the strain of bending the sp hybridized carbon atoms substantially away from 180° has too great an energetic cost. This situation may be ameliorated by resorting to transition metal complexes of cycloheptynes, particularly the dicobalt hexacarbonyl complexes.[2]Alkyne hexacarbonyldicobalt complexes have bond angles which average *ca*. 140° at the alkynyl carbons; the resultant lower angle strain renders the cycloheptyne and cyclohexyne complexes thermally stable.[3]

In addition to the above reasons, cobalt cycloheptyne complexes are of interest due to the potential for applying the rich synthetic utility of cobalt–alkyne complexes[4–6] to seven membered ring systems. This potential is largely unexplored, however, as these systems have been prepared infrequently,[7,8] and their systematic synthesis and study has escaped report. Notably, the attempt to prepare systems of this type *via* a double Nicholas reaction using allyldimetal equivalent **1** and propargylic ether **2** met with complete failure.[9]



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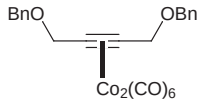

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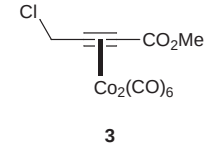
During our recent work involving silver mediated reactions of γ-chloro-alkynoate and -alkynone hexacarbonyldicobalt complexes,[10] we observed striking effects of the presence of an additional oxygen based function on the viability of propargyl alcohol or propargyl ether based Nicholas reactions. As a result, we believed that a stepwise reaction of **1** at the carbon bearing the chloride, manipulation of the carbonyl into a leaving group, and intramolecular allylsilane attack would give a cycloheptenyne complex.‡ Therefore, we tested the reaction of chloride **3** with **1** and $AgBF_4$ (0 °C, CH_2Cl_2), and to our surprise obtained a small amount of **4** as the sole condensation product. Compound **4** most probably results from the preferential loss of the internal trimethylsilyl group from the β-silyl cation intermediate, and allyldimetal equivalents with different electrofuges were investigated for their reactivity with **3**. Stannylsilane **5a**[11] gave more satisfactory results, and allylsilane **6a** was obtained as the major product, contaminated with vinylsilane **7a** (55%, **6a** : **7a** = 78 : 22). In this case the source of the isomeric impurity is believed to be Lewis acid mediated allylic rearrangement of the tin moiety in **5a** to give isomeric allyltin **5a′**;[12] despite this, recovered **5a** showed no evidence of **5a′**. Attempts to use systems with more bulky silyl groups gave improved regiochemical ratios in favour of the allylsilane product, at the expense of a satisfactory chemical yield.



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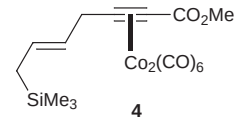

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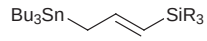
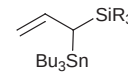
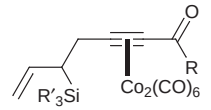


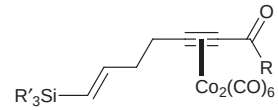
5a R = Me
5b R = Et



5a′ R = Me
5b′ R = Et



6a R′ = Me, R = OMe
6b R′ = Et, R = OMe
6c R′ = Et, R = Ph
6d R′ = Et, R = Me



7a R′ = Me, R = OMe
7b R′ = Et, R = OMe
7c R′ = Et, R = Ph
7d R′ = Et, R = Me

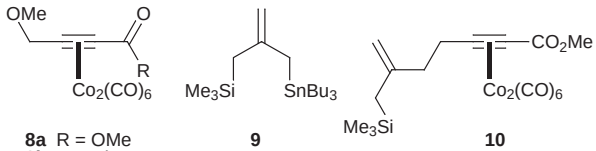
Based on the report from Jacobi's laboratory of the condensation of boron enolates with γ-methoxyalkynoate hexacarbonyldicobalt complexes,[13] we found that Bu_2BOTf (0 °C, CH_2Cl_2) was capable of inducing the condensation between propargyl ether **8a** with **5a** to give **6a**/**7a** (84%, **6a** : **7a** = 78 : 22). While regiochemical impurity **7a** was still present, the use of silylstannane **5b**[14] with **8a** was now possible, and allylsilane **6b** could be prepared in good yield with only a trace of **7b** (63%, **6b** : **7b** = 96 : 4; Table 1). Application of this protocol to phenyl ketone **8b** gave **6c** as the major product, with a more substantial amount of vinylsilane **7c** (73%, **6c** : **7c** = 82 : 18). The methyl ketone **8c** would undergo additional reaction of the alkyl ketone function in the presence of >1 equivalents of Bu_2BOTf, and optimum results for the formation of **6d** were obtained by inverting the order of reagent addition, and by conducting the reaction at −60 °C (39%, 77% based on recovered starting material, **6d** : **7d** = 92 : 8). Finally, silylstannane **9**[15] reacted smoothly with **8a** to give **10** in good yield (83%).

The carbonyl functions in **6** and **10** could be converted into a leaving group by low temperature (−78 °C) reduction with Bu^i_2AlH, and trapping of the resultant alkoxide with freshly distilled acetic anhydride at room temperature, affording acetates **11–12** in excellent yields. In the case of phenyl ketone **6c**, the acylation step was very slow, and the addition of sodium acetate with catalytic amounts of DMAP was required to give useful amounts of **11c**.

Table 1 Bu_2BOTf mediated condensations of allyldimetals **5** and **9** with **8**

Substrate	Allyldimetal	Product	Ratio	Yield (%)
8a	**5a**	**6a** + **7a**	78 : 22	84
8a	**5b**	**6b** + **7b**	96 : 4	63
8b	**5b**	**6c** + **7c**	82 : 18	73
8c	**5b**	**6d** + **7d**	92 : 8	39 (77)[a]
8a	**9**	**10**	—	83

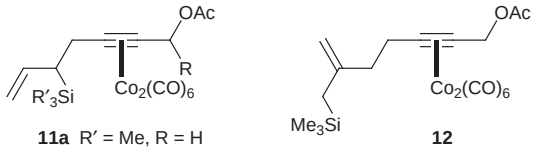
[a] Based on recovered starting material.



8a R = OMe
8b R = Ph

9

10



11a R′ = Me, R = H
11b R′ = Et, R = H
11c R′ = Et, R = Ph
11d R′ = Et, R = Me

12

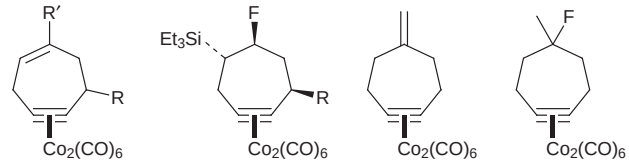
With the appropriately attached allylsilane and propargylic acetate functions in place, the ability of the substrates to form cycloheptyne complexes was investigated. Slow addition of a CH_2Cl_2 solution of **11** to a 0 °C CH_2Cl_2 solution of excess $BF_3{\cdot}Et_2O$ (final substrate concentration = 1 mM) rapidly afforded cycloheptenyne complexes **13**, as red–violet oils of good thermal stability, in excellent yields (Table 2). In the phenyl and methyl substituted cases **11c** and **11d**, trace amounts of fluorocycloheptyne complexes **14b** (8%) and **14c** (6%), respectively, were also isolated. In the case of substrate **12**, cyclization under these conditions afforded methylenecycloheptyne complex **15a** contaminated with a minor amount of the *endo* double bond isomer **15b** (46%, 87 : 13), along with desilylated fluorocycloheptyne complex **16** (44%). An alternative procedure which employed the slow addition of $BF_3{\cdot}Et_2O$ (5 equiv.) to a solution of **12** (1.5 mM) at 0 °C gave slightly enhanced amounts of **15a** + **15b** (55%, 90 : 10) and a small amount of **16** (8%).

The results demonstrate the facility with which the Nicholas reaction chemistry of cobalt stabilized γ-carbonyl cations can be applied to the preparation of cycloheptyne cobalt complexes. Further work in this area, including that on superior allyldimetal equivalents and one pot, [4 + 3] cycloaddition approaches to the

Table 2 Conversion of condensation products **6** and **10** to cycloheptenynes complexes **13** and **15**

Substrate	Acetate (Yield [%])	Cycloheptenyne (Yield [%])	Fluorocycloheptyne (Yield [%])
6a	**11a** (88)	**13a** (89)	—
6b	**11b** (90)	**13a** (87)	—
6c	**11c** (84[a])	**13b** (84)	**14b** (8)
6d	**11d** (88)	**13c** (85)	**14c** (6)
10	**12** (90)	**15a** + **b** (46) [87 : 13][b]	**16** (44)

[a] DMAP (0.2 equiv.) and NaOAc (excess) added during acylation step. [b] Numbers in square brackets represent the **15a** : **b** ratio.



13a R = H, R′ = H
13b R = Ph, R′ = H
13c R = Me, R′ = H
15b R = H, R′ = CH_3

14a R = Ph
14b R = Me

15a

16

complexes, and the synthetic applications of these compounds are in progress and will be reported in due course.

Notes and References

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‡ This represents an *endo–trig* variant of the Schreiber group ring closure step.[7]

1 A. Krebs and J. Wilke, *Top. Curr. Chem.*, 1983, **109**, 189; H. Meier, *Adv. Strain Org. Chem.*, 1991, **1**, 215.
2 M. J. Went, *Adv. Organomet. Chem.*, 1997, **41**, 69.
3 The stabilization of other strained alkynes also has been accomplished by complexation to the hexacarbonyldicobalt unit; see Y. Rubin, C. B. Knobler and F. Diederich, *J. Am. Chem. Soc.*, 1990, **112**, 4966; M. H. Haley and B. L. Langsdorf, *Chem. Commun.*, 1997, 1121.
4 R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, 1974, **12**, 323.
5 A. J. M. Caffyn and K. M. Nicholas, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, ed. L. S. Hegedus, Pergamon, Oxford, 1995, vol. 12, ch. 7.1; K. M. Nicholas, *Acc. Chem. Res.*, 1987, **20**, 207.
6 N. E. Schore, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, ed. L. S. Hegedus, Pergamon, Oxford, 1995, vol. 12, ch. 7.2; N. E. Schore, *Org. React.*, 1991, **40**, 1; N. E. Schore, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, ed. L. A. Paquette, Pergamon, Oxford, 1991, vol. 5, ch. 9.1; N. E. Schore, *Chem. Rev.*, 1988, **88**, 1081.
7 S. L. Schreiber, M. T. Klimas and T. Sammakia, *J. Am. Chem. Soc.*, 1986, **108**, 3128; T. Nakamura, T. Matsui, K. Tanino and I. Kuwajima, *J. Org. Chem.*, 1997, **62**, 3032.
8 N. E. Schore and S. D. Najdi, *J. Org. Chem.*, 1987, **52**, 5296; M. Isobe, C. Yenjai and S. Tanaka, *Synlett*, 1994, 916; S. Hosokawa and M. Isobe, *Synlett*, 1995, 1179.
9 S. Takano, T. Sugihara and K. Ogasawara, *Synlett*, 1992, 70.
10 C. S. Vizniowski, J. R. Green, T. L. Breen and A. V. Dalacu, *J. Org. Chem.*, 1995, **60**, 7496.
11 G. E. Keck and D. R. Romer, *J. Org. Chem.*, 1993, **58**, 6083.
12 M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987, pp. 216–218; A. Yanagisawa, A. Ishiba, H. Nakashima and H. Yamamoto, *Synlett*, 1997, 88.
13 P. A. Jacobi, S. C. Buddhu, D. Fry and S. Rajeswari, *J. Org. Chem.*, 1997, **62**, 2894.
14 Prepared in 90% yield, as adapted from the procedure of J. M. Muchowski, R. Naef and M. L. Maddox, *Tetrahedron Lett.*, 1985, **26**, 5375.
15 Prepared in 60% yield by the stannylation of 2-chloromethyl-3-trimethylsilylprop-1-ene according to S. Chandrasekhar, S. Latour, J. D. Wuest and B. Zacharie, *J. Org. Chem.*, 1983, **48**, 3810.

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