Journal of Organometallic Chemistry, 439 (1992) 189–199
Elsevier Sequoia S.A., Lausanne

JOM 22881

The synthesis of dimetallic thioalkyne complexes of cobalt and molybdenum

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(Received March 25, 1992)

Abstract

Treatment of $[Co_2(\mu\text{-}HOCR'_2C{\equiv}CCR'_2OH)(CO)_6]$ with an excess of RSH in the presence of $HBF_4 \cdot OEt_2$ affords $[Co_2(\mu\text{-}RSCR'_2C{\equiv}CCR'_2SR)(CO)_6]$ (R' = H, R = Et, ^{n}Bu, ^{t}Bu, Ph, Bz; R' = Me, R = Et), which undergo substitution with bis(diphenylphosphino)methane (dppm) to give $[Co_2(\mu\text{-}RSCR'_2C{\equiv}CCR'_2SR)(\mu\text{-dppm})(CO)_4]$. Similar treatment of $[MoCo(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_5Cp]$ and $[Mo_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_4Cp_2]$ with EtSH gives $[MoCo(\mu\text{-}EtSCH_2C{\equiv}CCH_2SEt)(CO)_5Cp]$ and $[Mo_2(\mu\text{-}EtSCH_2C{\equiv}CCH_2SEt)(CO)_4Cp_2]$, respectively. Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with a small excess of RSH (R=Et or Ph), *ca.* two equivalents, affords $[Co_2(\mu\text{-}HOCH_2C{=}CCH_2\text{-}SR)(CO)_6]$, while reaction with only one equivalent of EtSH additionally gives an ether-bridged system containing two hexacarbonyldicobalt units, $[Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OCH_2C{\equiv}CCH_2SEt)\text{-}Co_2(CO)_6]$. Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2SEt)(CO)_6]$ with half an equivalent of $HBF_4 \cdot OEt_2$ affords $[Co_2(CO)_6(EtSCH_2C{\equiv}CCH_2OCH_2C{\equiv}CCH_2SEt)Co_2(CO)_6]$. Attempted preparation of mixed thioether complexes results in a mixture of products, and a mechanism is proposed for thioether scrambling. The IR, NMR and mass spectra of the new compounds are reported and discussed.

Introduction

The synthetic utility of the hexacarbonyldicobalt stabilized propargyl cation (**1**) has been established for sometime and continues to attract a considerable amount of interest [1]. Cation **1** reacts with a wide variety of nucleophiles in which attack by the nucleophile occurs at the propargylic carbon, providing a versatile propargylation method when followed by mild oxidative demetalation. Although less extensively studied, several non-carbon-centred nucleophiles have been found to react with **1**. These include water to regenerate the parent alcohol [2], hydride to form alkylalkynes [3], alcohols to form ethers [2], and primary and secondary amines to afford propargylated amine complexes [4]. Reaction of **1** with pyridine, phosphines or thioethers affords a series of cationic derivatives, $[Co_2(\mu\text{-}HC{\equiv}CCH_2nuc)(CO)_6]^+$, additionally stabilized by attachment of the incoming nucleophile to the propargylic carbon [5].

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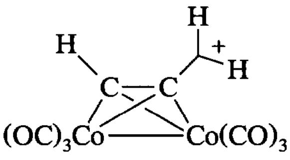

(1)

Propargyl cation chemistry is also known for $[M_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_4L_2]$ (M = Mo or W, L = Cp [6]; M = Mo, L = Cp′ [7]) and $[MCo(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_5]$ (M ≡ MoCp [8,9] or WCp′ [9]) and for mixed dicobalt or dimolybdenum ferrocene species [10]. Relatively little is known about 2-butyne-1,4-diol derivatives, for which there is the possibility of functionalization at both positions α to the acetylenic bond. Reduction of $[Co_2(\mu\text{-}HOCR_2C{\equiv}CCR_2OH)(CO)_6]$ with $NaBH_4$ in the presence of trifluoroacetic acid affords $[Co_2(\mu\text{-}HCR_2C{\equiv}CCR_2H)(CO)_6]$ [3]. In the case of $[Mo_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_4Cp_2]$, the corresponding dication $[Mo_2(\mu\text{-}CH_2C{\equiv}CCH_2)(CO)_4Cp_2]^{2+}$ has been isolated, and found to undergo hydrolysis to the parent diol, while reduction with $NaBH_4$ affords the 2-butyne adduct $[Mo_2(\mu\text{-}MeC{\equiv}CMe)(CO)_4Cp_2]$ [11].

It is not always necessary to isolate **1**, as in many cases it can be generated *in situ* in the presence of the nucleophile by the addition of a Lewis [12] or Brønsted [8] acid. For example, reaction of menthol with $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ occurs in the presence of $HBF_4 \cdot OEt_2$ and of activated 4 Å molecular sieves to afford $[Co_2(\mu\text{-}HC{\equiv}CCH_2O\text{–menthyl})(CO)_6]$ [8]. Our interest in dithioalkyne complexes as chelating ligands for low valent metal centres [13] led us to extend this methodology to thiols, and in this paper we describe the synthesis of dicobalt, dimolybdenum and cobalt-molybdenum dithioalkyne complexes from the corresponding 2-butyne-1,4-diol precursors. It has been previously postulated that thioalkyne hexacarbonyldicobalt complexes should be stable molecules [14].

Results and discussion

Treatment of $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ with an excess of EtSH in the presence of $HBF_4 \cdot OEt_2$ affords $[Co_2(\mu\text{-}HC{\equiv}CCH_2SEt)(CO)_6]$ (**2**) in 84% yield (see Experimental section). Analytical and IR data for the new compounds are given in Table 1. The solution IR spectrum of **2** recorded in light petroleum is typical of $[Co_2(\mu\text{-alkyne})(CO)_6]$ derivatives [15,16] and has absorptions *ca.* 2 cm^{-1} lower than those of $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ [17], reflecting the change from the alcohol to the less electronegative thioether substituent. The ^1H and ^{13}C NMR spectra (Table 2) are also readily interpreted by comparison with the starting material [4]. The ^1H NMR spectrum contains resonances at δ 6.09 and δ 3.95, assigned to the terminal acetylenic proton and the methylene protons, respectively, as well as the expected multiplets for the ethyl group. The corresponding resonances in $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ appear at δ 6.07 and δ 4.80, the shift of *ca.* 1 ppm for the methylene resonance is again a reflection of the substitution of alcohol for thioether. The $^{13}C\text{-}\{^1H\}$ NMR spectrum is also unexceptional, with resonances due to the acetylenic group at δ 73.3 for the terminal carbon and δ 93.5 for the substituted carbon. The methylene adjacent to the acetylenic group

Table 1

Analytical [a] and physical data

Compound	Appearance	Yield (%)	ν_{max}(CO) (cm^{-1})	Analysis (%)	
				C	H
2	Red oil	84	2095w, 2057s, 2032s, 2027m, 2013w [b]	33.9(34.2)	2.0(2.1)
3a	Red oil	73	2092w, 2054vs, 2028s, 2009w [b]	–	–
3b	Red oil	67	2092w, 2054vs, 2028s, 2009w [b]	35.8(36.7)	2.5(2.6)
3c	Red oil	53	2091m, 2054s, 2028s, 2008w [b]	–	–
3d	Red oil	64	2092m, 2054vs, 2032s, 2026s, 2007w [b]	–	–
3e	Orange solid	43	2093m, 2056vs, 2034s, 2010w [b]	47.7(47.5)	2.5(2.5)
3f	Red oil	63	2092m, 2055s, 2030s, 2010(sh) [b]	–	–
3g	Red solid	78	2090m, 2053s, 2026s, 2010(sh) [b]	41.4(41.8)	4.3(4.3)
4a	Red oil	74	2094m, 2056s, 2031vs, 2013(sh), 1982vw [b]	32.8(34.6)	2.7(2.4)
4b	Red oil	36	2093m, 2056s, 2029s, 2013(sh), 1980vw [b]	42.1(41.4)	2.1(2.2)
5b	Red oil	33	2093m, 2057s, 2025s [b]	–	–
6a	Red/orange solid	76	2021m, 1991s, 1964m, 1945(sh) [c]	54.9(55.3)	4.3(4.2)
6b	Orange solid	60	2021m, 1991s, 1964m, 1945(sh) [c]	56.2(56.4)	4.6(4.6)
6c	Pink solid	86	2021m, 1991s, 1964m, 1945(sh) [c]	57.0(56.9)	5.3(5.3)
6d	Red solid	96	2021m, 1991s, 1964m, 1945(sh) [c]	59.6(59.5)	5.5(5.1)
6e	Red/orange solid	57	2025m, 1995s, 1968m, 1951(sh) [c]	60.5(60.5)	3.9(4.1)
6f	Purple solid	67	2022m, 1991s, 1965m, 1945(sh) [c]	61.8(61.8)	4.7(4.4)
7	Red solid	27	2051m, 2003s, 1982s, 1942m, 1890w(br) [c]	37.2(37.7)	2.5(2.5)
8	Red oil	56	2067w, 2053m, 2005vs, 1988s, 1979s, 1941m, 1899w [b]	–	–
9	Red solid	68	1993m, 1911s, 1838m [d]	43.4(43.4)	4.0(4.0)

[a] Calculated values are given in parentheses. [b] In light petroleum. [c] In dichloromethane. [d] In toluene.

resonates at δ 35.8, markedly to high field of the corresponding resonance at δ 63.4 in the starting material.

Compound **3a** was prepared by reaction of octacarbonyldicobalt with 2,7-dithiooct-4-yne, while compounds **3b–g** were prepared by treating [$Co_2(\mu$-$HOCR'_2C{\equiv}CCR'_2OH)(CO)_6$] (R' = H or Me) with an excess of the appropriate thiol in the presence of $HBF_4 \cdot OEt_2$. Compounds **3** were characterized in a similar manner to **2**. For solutions in light petroleum, only **3d** has all of the five expected IR absorptions clearly resolved, the others showing ν_6 and ν_2 as a single unresolved band [16]. The electronegative nature of the phenyl substituent produces a shift of *ca.* 2 cm^{-1} to higher wavenumber in the IR spectrum of **3e**, while the methylene resonance in the ^{1}H NMR spectrum at δ 4.17 is furthest downfield for any of the derivatives. The positive inductive effect of the methyl groups in **3g** produces a small shift of *ca.* 2 cm^{-1} to lower wavelength in the IR spectrum. We suggest that the formation of compounds **3b–g** occurs *via* sequential functionalization at the α carbon atoms. If the reactions are performed with only a small excess of thiol (*ca.* 2 equiv.) the compounds [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2SR)(CO)_6$] are isolated and have been characterized for R=Et (**4a**) and Ph (**4b**). Reaction of **4a**

Table 2

Hydrogen-1 and carbon-13 NMR data [a]

Compound	$^1H(\delta)$	$^{13}C(\delta)$ [b]
2	6.09 (s, 1H, CH); 3.95 (s, 2H, CH_2); 2.68 [q, 2H, CH_2Me, $J(HH) = 7$]; 1.31 [t, 3H, CH_3, $J(HH) = 7$]	199.6 (CO); 93.5 ($\mathit{C}CH_2$); 73.3 (CH); 35.8 (CH_2); 26.7 (CH_2Me); 14.4 (CH_3)
3a	4.15 (s, 4H, CH_2); 2.16 (s, 6H, CH_3)	198.3 (CO); 95.0 (C_2); 37.3 (CH_2); 15.4 (CH_3) [c]
3b	4.01 (s, 4H, CH_2); 2.72 [q, 4H, CH_2Me, $J(HH) = 7$]: 1.33 [t, 6H, CH_3, $J(HH) = 7$]	199.5 (CO); 95.7 (C_2); 36.3 (CH_2); 27.6 (CH_2Me); 14.7 (CH_3)
3c	3.99 (s, 4H, CCH_2); 2.72 [t, 4H, SCH_2, $J(HH) = 7$]; 2.0–0.8 (m, 14H, $CH_2CH_2CH_3$)	199.6 (CO); 95.9 (C_2); 36.7 ($C\mathit{C}H_2$); 33.5, 31.9, 22.1 ($SCH_2CH_2CH_2$); 13.7 (CH_3)
3d	4.00 (s, 4H, CH_2); 1.40 (s, 18H, CH_3)	199.6 (CO); 95.2 (C_2); 43.4 (CMe_3); 32.7 (CH_2); 30.9 (CH_3)
3e	7.34–7.18 (m, 10H, Ph), 4.17 (s, 4H, CH_2)	199.1 (CO); 136.1 (C_1, Ph); 129.1, 128.9 ($C_{2,3,5,6}$, Ph); 126.4 (C_4, Ph); 94.3 (C_2); 38.1 (CH_2)
3f	7.3–7.2 (m, 10H, Ph); 3.82 (s, 4H, CH_2); 3.79 (s, 4H, CH_2)	200.0 (CO); 138–127 (m, Ph); 95.2 (C_2); 37.7, 35.7 (CH_2)
3g	2.76 [q, 4H, CH_2, $J(HH) = 7$]; 1.76 (s, 12H, CH_3); 1.28 [t, 6H, $CH_2C\mathit{H}_3$, $J(HH) = 7$]	200.2 (CO); 107.3 (C_2); 48.6 (C); 32.8 (CH_3); 24.6 (CH_2); 14.4 ($CH_2\mathit{C}H_3$)
4a	4.82 [d, 2H, $C\mathit{H}_2OH$, $J(HH) = 5$]; 4.00 (s, 2H, CH_2S); 2.90 (br, s, 1H, $CH_2O\mathit{H}$,); 2.71 [q, 2H, CH_2Me, $J(HH) = 7$]; 1.32 [t, 3H, CH_3, $J(HH) = 7$]	199.5 (CO); 96.8, 94.2 (C_2); 63.5 (CH_2OH); 35.9 (CH_2S); 27.7 (CH_2Me); 14.7 (CH_3)
4b	7.7–7.2 (m, 5H, Ph); 4.48 (s, 2H, CH_2S); 4.42 [d, 2H, CH_2O, $J(HH) = 6$]; 1.84 [t, 1H, OH, $J(HH) = 6$]	199.2 (CO); 135.0 (C_1, Ph); 129.4, 129.2 ($C_{2,3,5,6}$, Ph); 127.0 (C_4, Ph); 97.2, 92.5 (C_2); 63.1 (CH_2OH); 38.3 (CH_2S)
5b	4.90 (s, 4H, OCH_2); 4.00 (s, 4H, CH_2S): 2.70 [q, 4H, CH_2Me, $J(HH) = 7$]; 1.31 [t, 6H, CH_3, $J(HH) = 7$]	199.4 (CO); 94.6, 92.7 (C_2); 72.0 (CH_2O); 36.1 (CH_2S); 27.5 (CH_2Me); 14.7 (CH_3)

6a	7.64–7.08 (m, 20H, Ph); 4.00 [t, 4H, SCH_2, J(PH) = 3]; 3.48 [t, 2H, PCH_2P, J(PH) = 11]; 2.20 (s, 6H, CH_3)	203.9 (CO); 137–128 (m, Ph); 95.5 (C_2); 41.5 [t, PCH_2P, J(PC) = 20]; 40.4 (SCH_2); 17.3 (CH_3)
6b	7.6–7.2 (m, 20H, Ph); 4.02 (s, 4H, CH_2), 3.48 [t, 2H, PCH_2P, J(PH) = 11]; 2.68 [q, 4H, CH_2Me, J(HH) = 7]; 1.30 [t, 6H, CH_3, J(HH) = 7]	205.0 (CO); 137–128 (m, Ph); 96.0 (C_2); 41.5 [t, PCH_2 P, J(PC) = 20]; 37.6 (SCH_2); 27.5 (CH_2Me); 14.9 (CH_3)
6c	7.4–7.2 (m, 20H, Ph); 3.99 (s, 4H, CCH_2); 3.45 [t, 2H, PCH_2P, J(PH) = 10]; 2.63 [t, 4H, CH_2, J(HH) = 3]; 1.6–1.3 (m, 8H, CH_2 CH_2); 0.91 [t, 6H, CH_3, J(HH) = 7]	205.1 (CO); 137–128 (m, Ph); 96.1 (C_2); 41.5 [t, PCH_2P, J(PC) = 20]; 38.1 (CCH_2); 33.4, 32.0, 22.1 (CH_2); 13.8 (CH_3)
6d	7.4–7.2 (m, 20H, Ph); 3.98 (s, 4H, CH_2); 3.45 [t, 2H, PCH_2P, J(PH) = 10]; 1.33 (s, 18H, CH_3)	205.1 (CO); 137–128 (m, Ph); 95.3 (C_2); 42.4 (CMe_3); 42.0 [t, PCH_2P, J(PC) = 20]; 34.0 (CH_2); 31.0 (CH_3)
6e	7.6–7.2 (m, 30H, Ph); 4.25 [t, 4H, CH_2, J(PH) = 3]; 3.45 [t, 2H, PCH_2P, J(PH) = 10]	204.7 (CO); 138–125 (m, Ph); 93.9 (C_2); 42.3 [t, PCH_2P, J(PC) = 20]; 39.7 (CH_2)
6f	7.6–7.0 (m, 30H, Ph); 3.92 [t, 4H, CH_2S, J(PH) = 3]; 3.81 (s, 4H, CH_2Ph); 3.40 [t, 2H, PCH_2P, J(PH) = 10]	205.0 (CO); 139–127 (m, Ph); 95.3 (C_2); 41.4 [t, PCH_2P, J(PC) = 19]; 37.9, 37.7 (CH_2)
7	5.41 (s, 5H, Cp); 4.83 (s, 4H, CH_2); 3.35 (s, 2H, OH)	224.4 [Mo(CO)]; 203.5 [Co(CO)]; 93.7 (C_2); 90.3 (Cp); 66.5 (CH_2)
8	5.46 (s, 5H, Cp); 4.12 (s, 4H, CH_2); 2.70 [q, 4H, CH_2Me, J(HH) = 7]; 1.31 [t, 6H, CH_3, J(HH) = 7]	225.4 [Mo(CO)]; 203.3 [Co(CO)]; 93.7 (C_2); 91.1 (Cp); 38.4 (CH_2); 27.6 (CH_2Me); 15.0 (CH_3)
9	5.39 (s, 10H, Cp); 4.10 (s, 4H, CH_2); 2.63 [q, 4H, CH_2Me, J(HH) = 7]; 1.27 [t, 6H, CH_3, J(HH) = 7] [d]	230.4 (CO); 92.5 (Cp); 82.2 (C_2); 41.2 (CH_2); 27.9 (CH_2Me); 15.5 (CH_3) [d]

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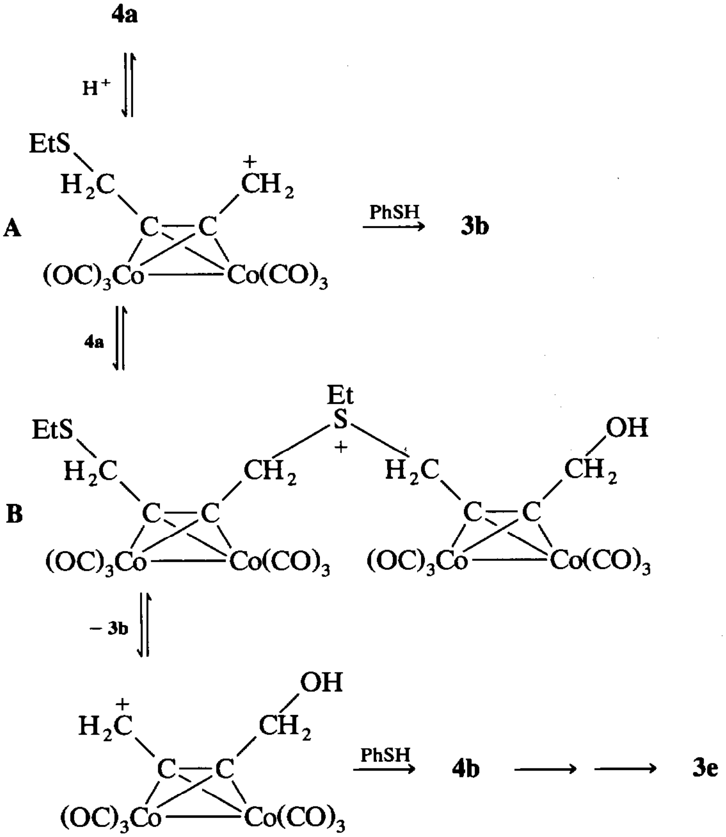
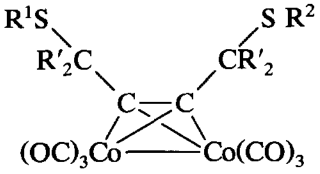
[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in $CDCl_3$ unless otherwise stated. [b] Hydrogen-1 decoupled. [c] Measured in C_6D_6. [d] Measured in CD_3COCD_3.

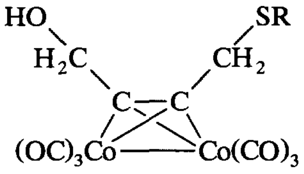


Scheme 1

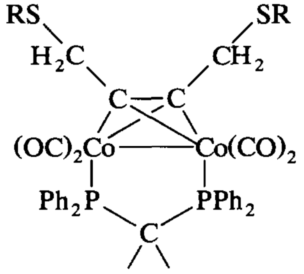
with an excess of EtSH in the presence of $HBF_4 \cdot OEt_2$ affords **3b** as expected. When the reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ was carried out with only 1 equiv. of EtSH, in the expectation of optimizing the yield of **4a**, it gave **4a** contaminated with **5a** (*ca.* 20%), and these were inseparable by column chromatography. The formation of ether-bridged systems has been reported previously in dicobalt alkyne chemistry [18] and in the related chemistry of 1,1′,2,2′-ferrocenetetramethanol [19]. Formation of **5a** presumably occurs via reaction of the intermediate cation **A** (see Scheme 1) derived from **4a** with an alcohol group of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$, rather than with EtSH. The presence of **5a** in the product mixture was revealed by the presence of additional resonances in the NMR spectra, although some of the expected resonances were obscured by overlap with those established for **4a**. In particular the $^{13}C\text{-}\{^1H\}$ NMR spectrum contains three of the four expected acetylenic resonances for **5a**, at δ 94.5, 92.2 and 90.5, as well as two resonances characteristic of the ether methylene groups, at δ 72.4 and δ 72.1 [20].



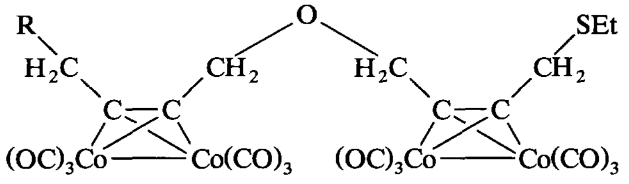
	R^1	R^2	R'
(3a)	Me	Me	H
(3b)	Et	Et	H
(3c)	^nBu	^nBu	H
(3d)	^tBu	^tBu	H
(3e)	Ph	Ph	H
(3f)	Bz	Bz	H
(3g)	Et	Et	Me
(3h)	Et	Ph	H
(3i)	Et	^tBu	H



	R
(4a)	Et
(4b)	Ph



	R
(6a)	Me
(6b)	Et
(6c)	^nBu
(6d)	^tBu
(6e)	Ph
(6f)	Bz



	R
(5a)	OH
(5b)	SEt

Reactions of **4a** with PhSH or **4b** with EtSH in the presence of $HBF_4 \cdot OEt_2$ afforded mixtures of **3b**, **3e** and **3h**, which could not be separated by column or thin layer chromatography. The FAB mass spectrum of the product mixture contains isotopic envelopes assigned to carbonyl loses from all three species, and all three species can be identified in the NMR spectra. Compound **3h** displays resonances due to the methylene groups adjacent to the acetylenic carbons in the ^1H NMR spectrum at δ 4.46 and 3.77, and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 38.6 and 36.0. Acetylenic resonances were also observed at δ 95.9 and 94.2. Reaction of **4a** with two equivalents of ^tBuSH in the presence of $HBF_4 \cdot OEt_2$ for 2 h afforded inseparable mixtures of **3b**, **3d** and **3i**. Compound **3i** was identified in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the mixture from additional acetylenic resonances of δ 96.1 and 94.8. Reaction of **3b** with excess ^tBuSH in the presence of $HBF_4 \cdot OEt_2$ results in only *ca.* 50% incorporation of ^tBuS after 24 h, as indicated by ^1H NMR spectroscopy. Protonation of the thioether functionality is therefore relatively slow, a result which is in accord which the slower protonation of methyl propargyl ether dicobalt complexes than of their propargyl alcohol analogues [12]. To account for the rapid scrambling of thioether groups we suggest the mechanism depicted in Scheme 1. The key intermediate **B** is a hexacarbonyldicobalt propargyl cation additionally stabilized by coordination of a thioether group of another dicobalt thioalkyne complex, as in the recently reported complexes $[Co_2(\mu\text{-}HC{\equiv}CCH_2SR_2)(CO)_6]^+$ [5]. Thioether transfer is effected by cleavage of the original C–S linkage.

Addition of 0.5 equiv. of $HBF_4 \cdot OEt_2$ to **4a** followed by neutralization and chromatography gave the coupled product **5b** in modest yield and several other trace products that were not characterized (see Experimental section). Compound **5b** is characterized by acetylenic resonances at δ 94.6 and 92.7 as well as an ether methylene resonance at δ 72.0, similar chemical shifts to those observed in **5a**. The FAB mass spectrum of **5b** shows isotope envelopes due to $[M - nCO]^+$ ($n = 3\text{–}7$, 9–12). Compound **5b** is presumably formed by reaction of intermediate **A** with **4a** followed by deprotonation.

Reaction of compounds **3a–f** with bis(diphenylphosphino)methane (dppm) in refluxing benzene gave good yields of **6a–f**, which were identified by comparison with other $[Co_2(\mu\text{-alkyne})(\mu\text{-dppm})(CO)_4]$ derivatives [21]. The dppm ligand in these derivatives occupies two equatorial sites, and the NMR spectra of compounds **6** indicate that an effective mirror plane containing the cobalt and phosphorus atoms is generated on the NMR time-scale, as observed previously [21]. FAB mass spectra of **6d–f** show isotope envelopes due to $[M - nCO]^+$ ($n = 0\text{–}4$). Attempts to prepare compounds **6** by treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-dppm})(CO)_4]$ with the appropriate thiol in the presence of $HBF_4 \cdot OEt_2$ were unsuccessful.

Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with $[CpMo(CO)_3]^-$ results in an isolobal replacement of a tricarbonylcobalt vertex to afford $[MoCo(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_5Cp]$ (**7**) [8], which reacts with an excess of EtSH in the presence of $HBF_4 \cdot OEt_2$ to afford $[MoCo(\mu\text{-}EtSCH_2C{\equiv}CCH_2SEt)(CO)_5Cp]$ (**8**), which was characterized spectroscopically. The FAB mass spectrum of **8** contains isotope envelopes assigned to $[M - nCO]^+$ ($n = 0\text{–}5$). Treatment of $[Mo_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_4Cp_2]$ in EtSH with $HBF_4 \cdot OEt_2$ affords $[Mo_2(\mu\text{-}EtSCH_2C{\equiv}CCH_2SEt)(CO)_4Cp_2]$ (**9**), whose NMR and IR spectra are in accord with those of other $[Mo_2(\mu\text{-alkyne})(CO)_4Cp_2]$ derivatives [22].

The results described in this paper illustrate how 2-butyne-1,4-diol complexes can be used as precursors of thioalkyne complexes. Coordination of thioether or alcohol groups to intermediate hexacarbonyldicobalt stabilized propargyl cations provides routes for thioether scrambling and ether-bridge formation.

Experimental

Reactions were carried out by Schlenk tube techniques under dry oxygen-free nitrogen. Dichloromethane was distilled over calcium hydride, light petroleum (b.p. 40–60°C), benzene and toluene over sodium, and diethyl ether and tetrahydrofuran over sodium-benzophenone. The IR spectra were recorded with a Mattson Alpha Centauri spectrophotometer. ^1H NMR spectra were recorded with JEOL GX 270 and PMX 60 instruments and $^{13}C\text{-}\{^1H\}$ spectra with a JEOL GX 270 instrument. The FAB mass spectra were recorded by the SERC mass spectrometry service at Swansea with a VG ZAB-E instrument. Elemental analyses were performed by Mr. A.J. Fassam at the University of Kent. The compounds $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ [4], $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ [23], $[Mo_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_4Cp_2]$ [11] and 2,7-dithiooct-4-yne [24] were prepared by published methods. The reagent $HBF_4 \cdot OEt_2$ consisted of an 85% solution in diethyl ether as supplied by Aldrich Chemicals. Analytical and other data for the new compounds are given in Tables 1 and 2.

Preparation of [$Co_2(\mu$-$HC{\equiv}CCH_2SEt)(CO)_6$] (2)

To a solution of [$Co_2(\mu$-$HC{\equiv}CCH_2OH)(CO)_6$] (0.18 g, 0.53 mmol) and EtSH (0.1 cm^3, 1.34 mmol) in CH_2Cl_2 (10 cm^3) were added three drops of $HBF_4 \cdot OEt_2$. After 1.25 h stirring, the acid was neutralized with an excess of $NaHCO_3$ and the solvent removed *in vacuo*. The residue was dissolved in light petroleum and the solution filtered through a plug of $MgSO_4$ (3 × 1.5 cm), then chromatographed on a Florisil column (10 × 1.5 cm). Elution with light petroleum produced a red band, which upon removal of the solvent *in vacuo* afforded [$Co_2(\mu$-$HC{\equiv}CCH_2SEt)(CO)_6$] as a red oil (0.17 g, 0.44 mmol). Compounds **3b–g** were prepared similarly by use of an approximately ten-fold excess of thiol.

Preparation of [$Co_2(\mu$-$MeSCH_2C{\equiv}CCH_2SMe)(CO)_6$] (3a)

A solution of [$Co_2(CO)_8$] (0.76 g, 2.22 mmol) and $MeSCH_2C{\equiv}CCH_2SMe$ (0.33 g, 2.26 mmol) in light petroleum (35 cm^3) was stirred for 1 h and then filtered through a Celite pad (1.5 × 3 cm). Reduction of the solvent volume *in vacuo* and cooling to 195 K afforded red/orange crystals, from which the supernatant liquid was decanted. When the crystals were allowed to warm to room temperature, they gave [$Co_2(\mu$-$MeSCH_2C{\equiv}CCH_2SMe)(CO)_6$] as a red oil (0.70 g, 1.62 mmol).

Preparation of [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2SEt)(CO)_6$] (4a)

To a solution of [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_6$] (0.70 g, 1.88 mmol) and EtSH (0.28 cm^3, 3.76 mmol) in CH_2Cl_2 (20 cm^3) were added two drops of $HBF_4 \cdot OEt_2$. After 2 h stirring, the acid was neutralized with excess $NaHCO_3$ and the solvent removed *in vacuo*. The residue was dissolved in light petroleum and the solution filtered through a plug of $MgSO_4$ (3 × 1.5 cm), then chromatographed on a Florisil column (10 × 1.5 cm). Elution with light petroleum produced a red band of **3b**, and elution with a light petroleum/CH_2Cl mixture (1:1) produced a second red band, which upon removal of the solvent *in vacuo* afforded [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2SEt)(CO)_6$] as a red oil (0.58 g, 1.39 mmol). A final band containing [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_6$] was removed from the column with THF. Compound **4b** was prepared similarly.

Reaction of [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2SEt)(CO)_6$] (4a) with ^{t}BuSH

To a solution of **4a** (0.13 g, 0.33 mmol) and ^{t}BuSH (0.07 cm^3, 0.67 mmol) in CH_2Cl_2 (10 cm^3) were added two drops of $HBF_4 \cdot OEt_2$. After 2 h stirring, the acid was neutralized with an excess of $NaHCO_3$ and the solvent removed *in vacuo*. The residue was dissolved in light petroleum and the solution filtered through a plug of $MgSO_4$ (3 × 1.5 cm^2), then chromatographed on a Florisil column (10 × 1.5 cm^2). Elution with light petroleum/CH_2Cl_2 (9:1) produced a red band, which upon removal of the solvent *in vacuo* left a mixture of **3b**, **3d** and **3i** as a red oil (0.08 g). Reactions of **4a** with PhSH and **4b** with EtSH were performed similarly.

Preparation of [$Co_2(CO)_6(EtSCH_2C{\equiv}CCH_2OCH_2C{\equiv}CCH_2SEt)Co_2(CO)_6$] (5b)

To a solution of **4a** (0.31 g, 0.75 mmol) in CH_2Cl_2 (20 cm^3) were added 4 Å molecular sieves and $HBF_4 \cdot OEt_2$ (0.069 cm^3, 0.40 mmol) and the mixture was stirred for 1.5 h. The acid was then neutralized with $NaHCO_3$, the solution filtered through a $MgSO_4$ plug (3×1.5 cm^2), and the solvent removed *in vacuo*. The residue was chromatographed on a Florisil column (15×1.5 cm^2). Elution with a light petroleum/CH_2Cl_2 mixture (20:1) afforded two minor bands followed by the major band. Removal of the solvent from this band *in vacuo* gave **5b** (0.10 g, 0.12 mmol). A fourth band was also obtained in too small a quantity to be characterized.

Preparation of [$Co_2(\mu$-$RSCH_2C{\equiv}CCH_2SR)(\mu$-dppm$)(CO)_4$] (6)

All the dppm substituted derivatives **6** were prepared by the same procedure, which is described in detail for **6e**. A solution of [$Co_2(\mu$-$PhSCH_2C{\equiv}CCH_2SPh)(CO)_6$] (**3e**) (0.24 g, 0.43 mmol) and dppm (0.17 g, 0.44 mmol) in benzene (15 cm^3) was refluxed for 0.5 h, after which the solution IR spectrum showed that all of **3e** had been consumed. The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (15×1.5 cm) with light petroleum/dichloromethane (2:1) as eluant. The red eluate was concentrated to *ca.* 2 cm^3 and addition of light petroleum (*ca.* 60 cm^3) afforded [$Co_2(\mu$-$PhSCH_2C{\equiv}CCH_2SPh)(\mu$-dppm$)(CO)_4$] (0.22 g, 0.25 mmol).

Preparation of [$MoCo(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_5Cp$] (7)

A solution of [$Mo_2(CO)_6Cp_2$] (0.49 g, 1.0 mmol) in THF (10 cm^3) was treated with an excess of Na/Hg amalgam. The mixture was stirred at room temperature until the solution lost the red colour associated with the dimer. Filtration gave a clear solution containing the anion, and after addition of [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_6$] (0.37 g, 1.0 mmol) the mixture was refluxed for 0.5 h. The solvent was then removed *in vacuo*, the residue extracted with diethyl ether, and the extract filtered through a plug of Florisil (3×1.5 cm). Chromatography of the extract on a Florisil column (10×1.5 cm^2), with diethyl ether as eluant gave a red eluate. Crystallization (Et_2O/light petroleum) afforded [$MoCo(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_5Cp$] (0.12 g, 0.27 mmol).

Preparation of [$MoCo(\mu$-$EtSCH_2C{\equiv}CCH_2SEt)(CO)_5Cp$] (8)

To a solution of [$MoCo(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_5Cp$] (0.15 g, 0.34 mmol) in CH_2Cl_2 (15 cm^3) were added EtSH (0.25 cm^3) and three drops of $HBF_4 \cdot OEt_2$. After 1 h stirring, the acid was neutralized with an excess of $NaHCO_3$ and the mixture filtered through a plug (3×1.5 cm) of $MgSO_4$. After removal of the solvent *in vacuo*, the residue was chromatographed on a Florisil column (10×1.5 cm^2), with a light petroleum/CH_2Cl_2 mixture (3:1) as eluant. Removal of the solvent *in vacuo* afforded [$MoCo(\mu$-$EtSCH_2C{\equiv}CCH_2SEt)(CO)_5Cp$] (0.10 g, 0.19 mmol).

Preparation of [$Mo_2(\mu$-$EtSCH_2C{\equiv}CCH_2SEt)(CO)_4Cp_2$] (9)

To a solution of [$Mo_2(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_4Cp_2$] (0.92 g, 1.77 mmol) in EtSH (3 cm^3) were added three drops of $HBF_4 \cdot OEt_2$. After 0.5 h stirring, an excess of $NaHCO_3$ was added to neutralize the acid and the solvent removed *in vacuo*. The residue was extracted with toluene and the extract filtered through a plug (3×1.5 cm) of $MgSO_4$ and then chromatographed on a silica gel column

(8 × 2 cm). Elution with toluene produced a red band, and removal of the solvent *in vacuo* afforded [$Mo_2(\mu$-$EtSCH_2C{\equiv}CCH_2SEt)(CO)_4Cp_2$] (0.73 g, 1.20 mmol).

Acknowledgements

Mr. A. Krebs is thanked for performing some preliminary experiments S.C.B. thanks the SERC for a studentship.

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