Synthesis and Reactivity of Dicobalt Stabilised But-2-yne-1,4-dicarbenium Ions

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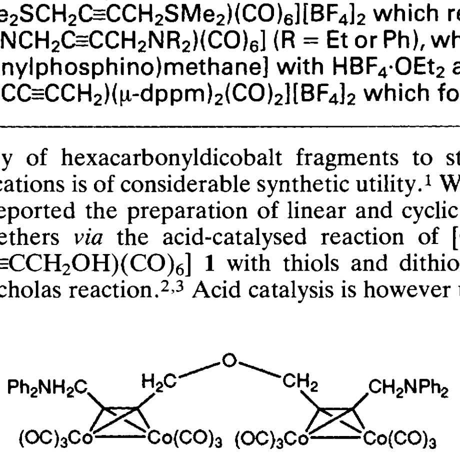
Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ in Me_2S with $HBF_4{\cdot}OEt_2$ affords the stable salt $[Co_2(\mu\text{-}Me_2SCH_2C{\equiv}CCH_2SMe_2)(CO)_6][BF_4]_2$ which reacts with secondary amines to afford $[Co_2(\mu\text{-}R_2NCH_2C{\equiv}CCH_2NR_2)(CO)_6]$ (R = Et or Ph), while treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-dppm})_2(CO)_2]$ [dppm = bis(diphenylphosphino)methane] with $HBF_4{\cdot}OEt_2$ affords a stable dicarbenium complex $[Co_2(\mu\text{-}H_2CC{\equiv}CCH_2)(\mu\text{-dppm})_2(CO)_2][BF_4]_2$ which forms adducts with pyridine and triphenylphosphine.

The ability of hexacarbonyldicobalt fragments to stabilise propynyl cations is of considerable synthetic utility.[1] We have recently reported the preparation of linear and cyclic acetylenic thioethers *via* the acid-catalysed reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ **1** with thiols and dithiols in a double Nicholas reaction.[2,3] Acid catalysis is however unsuitable for synthesising more basic amine difunctionalised alkynes. Monofunctionalised amine alkyne complexes have been prepared by reaction of $[Co_2(\mu\text{-}HC{\equiv}CCH_2)(CO)_6]BF_4$ or $[Mo_2(\mu\text{-}HC{\equiv}CCH_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]BF_4$ with primary and secondary amines.[4] In an attempt to prepare $[Co_2(\mu\text{-}Ph_2NCH_2C{\equiv}CCH_2NPh_2)(CO)_6]$ **2**, a large excess of $HBF_4{\cdot}OEt_2$ was added to a diethyl ether solution of **1** to form a red suspension which was washed with diethyl ether at −50 °C and then treated with $HNPh_2$. Work-up afforded a mixture of **2**, $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2NPh_2)(CO)_6]$ **3** and **4**.† This result indicates the possible intermediacy of $[Co_2(\mu\text{-}H_2CC{\equiv}CCH_2)(CO)_6]^{2+}$ and similar evidence has been obtained from the reaction of $[Co_2(\mu\text{-}PhCH_2OCH_2C{\equiv}CCH_2OCH_2Ph)(CO)_6]$ with nucleophiles in the presence of $BF_3{\cdot}OEt_2$ at low temperature.[5] A cleaner reaction would be expected if the intermediate dication could be isolated and purified. Although $[Mo_2(\mu\text{-}H_2CC{\equiv}CCH_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]^{2+}$ has been characterised,[6] so far $[Co_2(\mu\text{-}H_2CC{\equiv}CCH_2)(CO)_6]^{2+}$ has not been isolated. A bis(9-fluoreniumyl) ethyne ditetrafluoroborate-ethyne-hexacarbonyldicobalt complex has recently been reported and is found to be unstable at room temperature.[7]



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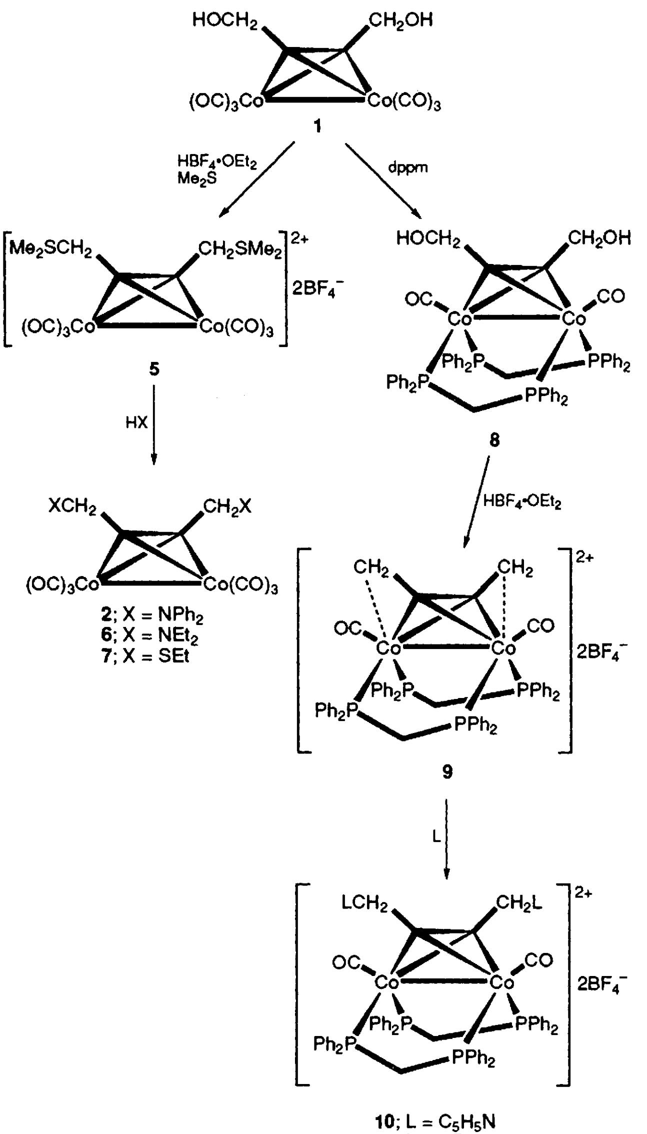

Scheme 1

It has been shown that $[Co_2(\mu\text{-}HC{\equiv}CCH_2)(CO)_6]BF_4$ can be stabilised by reaction with dimethyl sulfide to afford $[Co_2(\mu\text{-}HC{\equiv}CCH_2SMe_2)(CO)_6]BF_4$, which is however still reactive with respect to nucleophilic attack.[8] Protonation of **1** in SMe_2 with $HBF_4{\cdot}OEt_2$ affords $[Co_2(\mu\text{-}Me_2SCH_2C{\equiv}CCH_2SMe_2)(CO)_6][BF_4]_2$ **5** in high yield as a thermally stable orange solid (see Scheme 1) which can be stored in the air for over a year. Reaction of **5** with $HNPh_2$ affords **2**, while reactions with $HNEt_2$ and EtSH afford $[Co_2(\mu\text{-}Et_2NCH_2C{\equiv}CCH_2NEt_2)(CO)_6]$ **6**[9] and $[Co_2(\mu\text{-}EtSCH_2C{\equiv}CCH_2SEt)(CO)_6]$, **7**[2] respectively.

An alternative approach is to improve the ability of the dicobalt centres to stabilise positive charge by substitution with phosphine ligands. Protonation of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-dppm})_2(CO)_2]$ **8** [dppm = bis(diphenylphosphino)methane] with $HBF_4{\cdot}OEt_2$ affords $[Co_2(\mu\text{-}H_2CC{\equiv}CCH_2)(\mu\text{-dppm})_2(CO)_2][BF_4]_2$ **9** in high yield. The spectator role of the BF_4^- counterions was confirmed by the observation of a single resonance in the ^{19}F NMR spectrum. The ^1H NMR spectrum of **9** reveals that the $-CH_2^+$ group is not rotating on the NMR timescale as two distinct methylene resonances are observed and the presence of two signals in the $^{31}P\{^1H\}$ NMR spectrum indicates that migration between the cobalt centres is also slow. Reaction of compound **9** with pyridine or triphenylphosphine affords **10** and **11**, respectively.

In conclusion compound **5** is a stabilised dicarbenium complex and compound **9** are the first example of a stable dicarbenium dicobalt complex and both will provide new routes to difunctionalised alkynes.

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Footnote

† *Selected spectroscopic data*: Compound **2**: ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (m, 20H, Ph) and 5.24 (s, 4H, CH_2NPh_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.3 (CO), 147–118 (Ph), 94.6 (C_2), 55.8 (CH_2NPh_2). Compound **3**: ν_{CO}/cm^{-1} (CH_2Cl_2) 2088m, 2048vs and 2022s; ^{1}H NMR ($CDCl_3$) δ 7.3–7.0 (m, 10H, Ph), 5.24 (s, 2H, CH_2), 4.24 [d, 2H, CH_2OH, J_{HH} 6.6 Hz] and 1.37 [t, 1H, OH, J_{HH} 6.6 Hz]; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.4 (CO), 147–120 (Ph), 98.0 ($\equiv CCH_2OH$), 91.7 ($\equiv CCH_2NPh_2$), 63.1 (CH_2OH), 55.4 (CH_2NPh_2). EI mass spectrum: *m/z* 495, 467, 439, 411, 383, 355 ($M^+ - n$CO, n = 1–6). Compound **4**: ν_{CO}/cm^{-1} (light-petroleum ether) 2093m, 2056vs, 2032s and 2025s, ^{1}H NMR ($CDCl_3$) δ 7.3–6.9 (m, 20H, Ph), 5.18 (s, 4H, CH_2NPh_2) and 4.18 (s, 4H, CH_2O); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.3 (CO), 147–120 (Ph), 93.8, 92.3 (C_2), 71.5 (CH_2O), 55.1 (CH_2NPh_2); FAB mass spectrum: *m/z* 1029 (M^+ + H). Compound **5**: ν_{CO}/cm^{-1} (Me_3CN) 2110m, 2075s and 2049s; ^{1}H NMR (CD_3CN) δ 4.90 (s, 4H, CH_2) and 3.05 (s, 12H, Me); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 198.2 (CO), 82.9 (C_2), 49.9 (CH_2), 27.1 (Me). Compound **8**: ν_{CO}/cm^{-1} (KBr) 1915s and 1905s. Compound **9**: ν_{CO}/cm^{-1} (CH_2Cl_2) 2056m and 2038s; ^{1}H NMR (CD_2Cl_2) δ 7.72–6.98 (m, 40H, Ph), 6.13 (s br, 2H, CH_2), 5.44–5.39 (m, 2H, PCH_2P), 4.35 (s, br, 2H, CH_2), 4.29–4.14 (m, 2H, PCH_2P); $^{13}C\{^1H\}$ NMR (CD_3CN) δ 195.1 (CO), 137.0–128.4 (Ph), 123.0 [d of d, C≡C, J_{PC} 12 and 31 Hz], 86.3 (CH_2), 44.6 [t, PCH_2P, J_{PC} 23 Hz]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 34.4 (s br) and 9.9 (s br). Compound **10**: ν_{CO}/cm^{-1} (CH_2Cl_2) 1988s. Compound **11**: ν_{CO}/cm^{-1} (CH_2Cl_2) 1979s. FAB mass spectrum: *m/z* 1605 ($M^+ - BF_4$).

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