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Synthesis and reactions at Co–CH_2 and $C\equiv C$ bonds of cobalt-propargyl complexes

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Abstract

The first cobalt-propargyl complexes $RC\equiv CCH_2Co(CO)_3PPh_3$ (**1**: R = Me (**a**), Ph (**b**), CH_2Cl (**c**)) were prepared by reaction of $NaCo(CO)_3PPh_3$ with $RC\equiv CCH_2X$ (X = Cl or Br) in THF at ca. −20 °C. Also synthesized, by treatment of $NaCo(CO)_4$ in diethyl ether under CO at −20 to 0 °C with one equivalent of each PPh_3 and $RC\equiv CCH_2X$ in that order, were the first examples of metal acylpropargyl complexes, $RC\equiv CCH_2C(O)Co(CO)_3PPh_3$ (**2**). Both **1** and **2** were characterized by elemental analysis and IR and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectroscopy and shown to adopt C_{3v} structures. **1a**,**1b** undergo carbonylation to **2a**,**2b** in THF or CH_2Cl_2 solution at 0 °C under 1 atm of CO; the reverse reaction occurs at room temperature when Ar is passed into solutions of **2a**,**2b** in THF. The carbonylation reactions represent the first examples of insertion of CO into a propargyl carbon-to-metal linkage. **1a**,**1b** undergo [3 + 2] cycloaddition reactions with $(CN)_2C{=}C(CN)_2$ and SO_2 to afford $\overline{CH_2C(CN)_2C(CN)_2C(R){=}C}Co(CO)_3PPh_3$ (**3a**,**3b**) and $\overline{CH_2OS(O)C(Me){=}C}Co(CO)_3PPh_3$ (**4a**), respectively.

Introduction

Propargyl complexes, $RC\equiv CCH_2ML_n$, are known for a number of transition metals [1,2]. These compounds undergo interesting reactions at the $C\equiv C$ bond when treated with electrophilic reagents [1,3]. For instance, protonation of $RC\equiv CCH_2ML_n$ leads to the formation of the cationic allene complexes $[(\eta^2\text{-}CH_2{=}C{=}CHR)ML_n]^+$, whereas addition of unsaturated electrophiles such as SO_2, $(CN)_2C{=}C(CN)_2$-(TCNE), $(CF_3)_2CO$, and $p\text{-}MeC_6H_4SO_2NCO$ (E = Nu; E = electrophilic part, Nu = nucleophilic part) affords [3 + 2] cycloaddition products, $\overline{CH_2NuEC(R){=}C}ML_n$. Recently, propargyl complexes have been employed as reagents in the synthesis of heterobinuclear and -trinuclear metal-alkyne and -allenyl complexes [4–6].

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In view of the attention that has been accorded this class of compounds, it is surprising that there are no reports of the synthesis of propargyl complexes of cobalt tetracarbonyl and derivatives. Alkyl and related complexes of cobalt of general composition $RCo(CO)_x(PR'_3)_{4-x}$ have been known for a number of years [7–9]. They have been the subject of intensive studies owing to their importance in several stoichiometric and catalytic processes, including hydroformylation. Carbonylation and isomerization reactions have received much attention in that context.

In this paper we report the synthesis of the first cobalt-propargyl complexes, $RC\equiv CCH_2Co(CO)_3PPh_3$, and some of their reactions. Reactions of the $RC\equiv CCH_2Co$ fragment feature migratory insertion of CO into the $Co–CH_2$ bond, which is the first example of such an insertion into a propargyl carbon-to-metal linkage.

Experimental

General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of purified Ar or CO by use of standard procedures [10]. Elemental analyses for C, H, and N were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cobalt was analyzed [11] after oxidation with a mixture of H_2O_2 and HNO_3. Chromatographic separations and purifications were effected on columns packed with alumina (Brockman I). Infrared (IR) spectra were recorded on a Perkin–Elmer Model 283B grating spectrophotometer or a Mattson Cygnus-25 Fourier-transform spectrometer in a 0.047-mm solution cell with CaF_2 windows and were calibrated with polystyrene. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM-250 or AM-500 spectrometer, and the chemical shifts are given in ppm downfield from the internal standard Me_4Si. $^{31}P\{^1H\}$ NMR spectra were recorded on the Bruker AM-250, with the chemical shifts being referenced to 85% H_3PO_4.

Materials

Solvents were distilled as previously described [4]. $Co_2(CO)_8$ was crystallized first from CH_2Cl_2 and then from hexane under an atmosphere of CO. Colorless solutions of $NaCo(CO)_4$ in diethyl ether were prepared from $Co_2(CO)_8$ and 1% Na/Hg [12]. Light yellow solutions of $NaCo(CO)_3PPh_3$ in THF were obtained by reaction of $Co_2(CO)_6(PPh_3)_2$ [13] with 1% Na/Hg according to the literature [14]. The concentrations of these solutions were determined by Co analysis.

2-Butyne-1-ol was obtained from Farchan. 3-Phenyl-2-propyne-1-ol was synthesized by reaction of $PhC\equiv CH$ with n-BuLi and addition of paraformaldehyde [15]. Both alcohols were converted to the corresponding bromides, $MeC\equiv CCH_2Br$ and $PhC\equiv CCH_2Br$, respectively, by action of PBr_3 [16]. Commercial 1,4-dichloro-2-butyne (Farchan) was distilled under Ar prior to use. Tetracyanoethylene (TCNE), from Aldrich, was freshly sublimed in vacuo at 70 °C. Anhydrous grade SO_2, from Matheson, was dried with P_4O_{10}. Other reagents were used as received from various commercial sources.

Preparation of $RC\equiv CCH_2Co(CO)_3PPh_3$ (1)

All complexes were prepared by dropwise addition of an equimolar amount of $RC\equiv CCH_2X$ (X = Cl or Br) to a stirred solution of $NaCo(CO)_3PPh_3$ in THF at ca.

$-20\,^\circ$C under Ar. The addition of $RC{\equiv}CCH_2X$ resulted in the formation of a white or yellow solid, and stirring was continued until the IR ν(CO) spectrum of the solution showed a complete disappearance of $NaCo(CO)_3PPh_3$ *. The reaction solution was then chromatographed on a 20 × 1-cm column of alumina at 0 °C under Ar eluting with diethyl ether. The first deep yellow band was collected and concentrated. Addition of pentane at low temperature (-30 to 0 °C) induced crystallization of **1**. Specific details of synthesis, yields, spectroscopic properties, and chemical analysis of various cobalt-propargyl complexes are given below.

(i) $MeC{\equiv}CCH_2Co(CO)_3PPh_3$ (1a). A THF solution of $NaCo(CO)_3PPh_3$ (10 ml, 0.284 *M*) was allowed to react with $MeC{\equiv}CCH_2Br$ (0.274 ml, 3.0 mmol) for 15 min. Chromatography and crystallization at $-30\,^\circ$C yielded 1.12 g (86%) of **1a** as a yellow solid: IR (THF) ν(CO) 2036 (vw), 1972 (vs), 1965 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2, 250.1 MHz) δ 7.48 (m, 3Ph), 2.36 (m, CH_2), 1.80 (m, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 200.84 (d, *J*(PC) = 20.0 Hz, 3CO), 134.16–128.82 (3Ph), 88.10 (d, *J*(PC) = 4.0 Hz, CCH_2), 79.05 (d, *J*(PC) = 3.8 Hz, *C*Me), 4.63 (Me), -7.20 (d, *J*(PC) = 21.4 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.2 MHz) δ 57.8. Anal. Found: C, 65.20; H, 4.36. $C_{25}H_{20}CoO_3P$ calcd: C, 65.51; H, 4.39%.

(ii) $PhC{\equiv}CCH_2Co(CO)_3PPh_3$ (1b). The product was obtained (51% yield) as a yellow solid from reaction of $NaCo(CO)_3PPh_3$ with $PhC{\equiv}CCH_2Br$ for 2 h, followed by chromatography and crystallization at 0 °C: IR (THF) ν(C≡C) 2193 (vw), ν(CO) 2036 (vw), 1972 (vs), 1964 (vs), ν(C=C, Ph) 1597 (vw) cm^{-1}; ^1H NMR (CD_2Cl_2, 500.1 MHz) δ 7.5–7.2 (m, 4Ph), 2.58 (d, *J*(PH) = 2.71 Hz, CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 200.49 (d, *J*(PC) = 20.0 Hz, 3CO), 134.44–127.08 (4Ph), 100.43 (CCH_2), 84.32 (d, *J*(PC) = 3.7 Hz, *C*Ph), -7.81 (d, *J*(PC) = 21.0 Hz, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 101.2 MHz) δ 57.9. Anal. Found: C, 68.77; H, 4.44. $C_{30}H_{22}CoO_3P$ calcd.: C, 69.24; H, 4.26%.

(iii) $ClCH_2C{\equiv}CCH_2Co(CO)_3PPh_3$ (1c). The title complex was obtained (13% yield) as a yellow solid from reaction of $NaCo(CO)_3PPh_3$ with $ClCH_2C{\equiv}CCH_2Cl$ under similar conditions: IR (THF) ν(CO) 2038 (vw), 1978 (vs), 1960 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2, 250.1 MHz) δ 7.43 (m, 3Ph), 4.21 (s, CH_2Cl), 2.53 (s, CH_2Co); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.9 MHz) δ 200.4 (d, *J*(PC) ~ 18 Hz, 3CO), 134–128 (3Ph), 93.5 (one or both C≡), 30.4 (CH_2Cl), -4.85 (d, *J*(PC) = 18 Hz, CH_2Co); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.2 MHz) δ 57.1.

Preparation of $RC{\equiv}CCH_2C(O)Co(CO)_3PPh_3$ (2)

An equimolar amount of first PPh_3 and then $RC{\equiv}CCH_2X$ was added to a cold (-20 to 0 °C) stirred solution of $NaCo(CO)_4$ in diethyl ether under CO, resulting in a slow precipitation of a dirty yellow solid. Stirring was continued until the IR ν(CO) spectrum of the solution [17] revealed that the $NaCo(CO)_4$ has been completely consumed. The reaction solution was then filtered, and the filtrate was concentrated and treated with pentane. Cooling at ca. $-75\,^\circ$C resulted in the precipitation of product **2**. Specific details of synthesis, yields, spectroscopic properties, and elemental analysis of complexes **2a**–**2c** are given below.

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* FT IR ν(CO) bands of a 0.04 *M* solution of $NaCo(CO)_3PPh_3$ in THF recorded in a 0.047-mm CaF_2 cell are 1938.6 (0.13, sh), 1930.2 (0.30), 1854.4 (0.62), 1842.9 (0.29, sh, and 1806.5 (0.27, br) cm^{-1} (absorbance in parentheses).

(i) $\mathit{MeC{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ *(**2a**).* Equimolar amounts of $\mathrm{NaCo(CO)_4}$ (0.0756 *M*, 4.16 mmol), $\mathrm{MeC{\equiv}CCH_2Br}$ (0.38 ml, 4.16 mmol), and $\mathrm{PPh_3}$ (1.09 g, 4.16 mmol) in 55 ml of diethyl ether were reacted at −5 °C for 4 h. Crystallization from 30 ml of 2 : 1 pentane–diethyl ether yielded 1.40 g (70%) of **2a** as a yellow solid: IR (THF) ν(CO) 2046 (w), 1984 (vs), 1964 (vs), 1669 (m) $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 500.1 MHz) δ 7.56–7.40 (m, 3Ph), 3.74 (s, $\mathrm{CH_2}$), 1.86 (s, Me); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 125.8 MHz) δ 236.25 (d, *J*(PC) = 35.33 Hz, Co*C*(O)$\mathrm{CH_2}$), 198.76 (d, *J*(PC) = 20.62 Hz, 3CO), 133.15, 132.57, 131.12, 129.00 (3Ph), 81.33, 73.59 (C≡C), 52.22 (d, *J*(PC) = 26.5 Hz, $\mathrm{CH_2}$), 3.72 (Me); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 101.2 MHz) δ 48.9.

(ii) $\mathit{PhC{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ *(**2b**).* The product was obtained by reaction of $\mathrm{NaCo(CO)_4}$ with $\mathrm{PhC{\equiv}CCH_2Br}$ and $\mathrm{PPh_3}$ at −20 to 0 °C for 4 h. Crystallization was effected from 40 ml of 1 : 1 pentane–diethyl ether to furnish **2b** as a deep yellow solid in 70% yield. (Combining $\mathrm{PhC{\equiv}CCH_2Br}$ and $\mathrm{PPh_3}$ in THF at room temperature resulted in the formation of a yellow precipitate that reacted smoothly with $\mathrm{NaCo(CO)_4}$ at 0 °C to give the same product.): IR (THF) ν(C≡C) 2188 (vw), ν(CO) 2046 (w), 1986 (vs), 1967 (vs), 1667 (m) $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 500.1 MHz) δ 7.5–7.4 (m, 4Ph), 3.88 (s, $\mathrm{CH_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 125.8 MHz) δ 235.60 (d, *J*(PC) = 36.36 Hz, Co*C*(O)$\mathrm{CH_2}$), 198.78 (d, *J*(PC) = 21.16 Hz, 3CO), 133.52–123.59 (4Ph), 86.24, 84.99 (C≡C), 52.22 (d, *J*(PC) = 25.97 Hz, $\mathrm{CH_2}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 0 °C, 101.2 MHz) δ 48.9. Anal. Found: C, 67.15; H, 4.28. $\mathrm{C_{31}H_{22}CoO_4P}$ calcd.: C, 67.89; H, 4.04%.

(iii) $\mathit{ClCH_2C{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ *(**2c**).* Reaction of $\mathrm{NaCo(CO)_4}$ with $\mathrm{ClCH_2C{\equiv}CCH_2Cl}$ and $\mathrm{PPh_3}$ at 0 °C for 24 h followed by crystallization from 100 ml of 1 : 1 pentane–diethyl ether afforded a tan solid in 14% yield: IR ($\mathrm{CH_2Cl_2}$) ν(CO) 2046 (w), 1986 (vs), 1967 (vs), 1662 (m) $\mathrm{cm^{-1}}$; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 101.2 MHz) δ 48.8. Anal. Found: C, 60.44; H, 4.27. $\mathrm{C_{26}H_{18}ClCoO_4P}$ calcd.: C, 59.96; H, 3.68%.

Decarbonylation of $\mathit{RC{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ *where R = Me or Ph (**2a**, **2b**)*

A solution of **2a** (0.555 g) in THF (6 ml) at room temperature was purged with argon for 1 h and then chromatographed on alumina eluting with diethyl ether. A dark yellow band was removed from the column, concentrated to 5 ml, and treated with 5 ml of pentane. The resulting solution was cooled at −30 °C for 12 h to give 0.410 g (78% yield) of the yellow crystalline $\mathrm{MeC{\equiv}CCH_2Co(CO)_3PPh_3}$ (**1a**).

A similar procedure was used to obtain $\mathrm{PhC{\equiv}CCH_2Co(CO)_3PPh_3}$ (**1b**) from **2b** in 43% yield. Both products **1** were characterized spectroscopically.

Carbonylation of $\mathit{RC{\equiv}CCH_2Co(CO)_3PPh_3}$ *where R = Me or Ph (**1a**, **1b**)*

Stirring a 0.02 *M* solution of **1a** in THF or $\mathrm{CH_2Cl_2}$ at 0 °C under an atmosphere of CO for 24 or 90 h, respectively, afforded $\mathrm{MeC{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ (**2a**) as ascertained by IR spectroscopy.

Similarly, $\mathrm{PhC{\equiv}CCH_2C(O)Co(CO)_3PPh_3}$ (**2b**) was obtained from **1b** and CO. The acyl products **2** were not isolated.

Reaction of $\mathit{RC{\equiv}CCH_2Co(CO)_3PPh_3}$ *where R = Me or Ph (**1a**, **1b**) with* $\mathit{(CN)_2C{=}C(CN)_2}$ *(TCNE)*

To a solution of **1a** (0.341 g, 0.745 mmol) in THF (2.5 ml) at 0 °C under Ar, TCNE (0.0955 g, 0.745 mmol), also in THF (2.5 ml), was added in one portion with stirring. In ca. 5 min, the dark yellow reaction mixture changed color to pale greenish yellow, and the IR spectrum showed only new ν(CO) bands at 2052 (vw) and 1987 (vs, br) cm^{-1}. The mixture was concentrated to ca 2 ml and chromatographed on alumina eluting with diethyl ether at 0 °C. A pale yellow band was collected, and the solvent was evaporated to leave 0.245 g (56% yield) of a white solid, $\overline{CH_2C(CN)_2C(CN)_2C(Me)=C}Co(CO)_3PPh_3$ (**3a**): FT IR (0.040 *M*, THF (absorbance)) ν(CO) 2053.9 (0.026), 1983.9 (0.751), 1982.4 (0.758) cm^{-1}; ^1H NMR (CD_2Cl_2, 500.1 MHz) δ 7.60–7.45 (m, 3Ph), 3.81 (s, CH_2), 2.23 (s, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 197.26 (d, J(PC) = 23.2 Hz, 3CO), 148.10 (d, J(PC) = 27.6 Hz, =CCo), 133.35 (d, J(PC) = 11.15 Hz, 6 *o*-C of Ph), 132.38 (d, J(PC) = 50.58 Hz, 3 *ipso*-C of Ph), 132.04 (3*p*-C of Ph), 129.56 (d, J(PC) = 10.25 Hz, 6*m*-C of Ph), 128.58 (d, J(PC) = 3.30 Hz, *C*Me), 112.44, 110.79 (4CN), 56.83 (d, J(PC) = 3.80 Hz, CH_2), 16.63 (Me); $^{31}P\{^1H\}$ NMR (THF, 101.2 MHz) δ 54.28. Anal. Found: C, 63.94; H, 3.86; N, 9.18; Co, 10.14. $C_{31}H_{20}CoN_4O_3P$ calcd.: C, 63.49; H, 3.44; N, 9.55; Co, 10.05%.

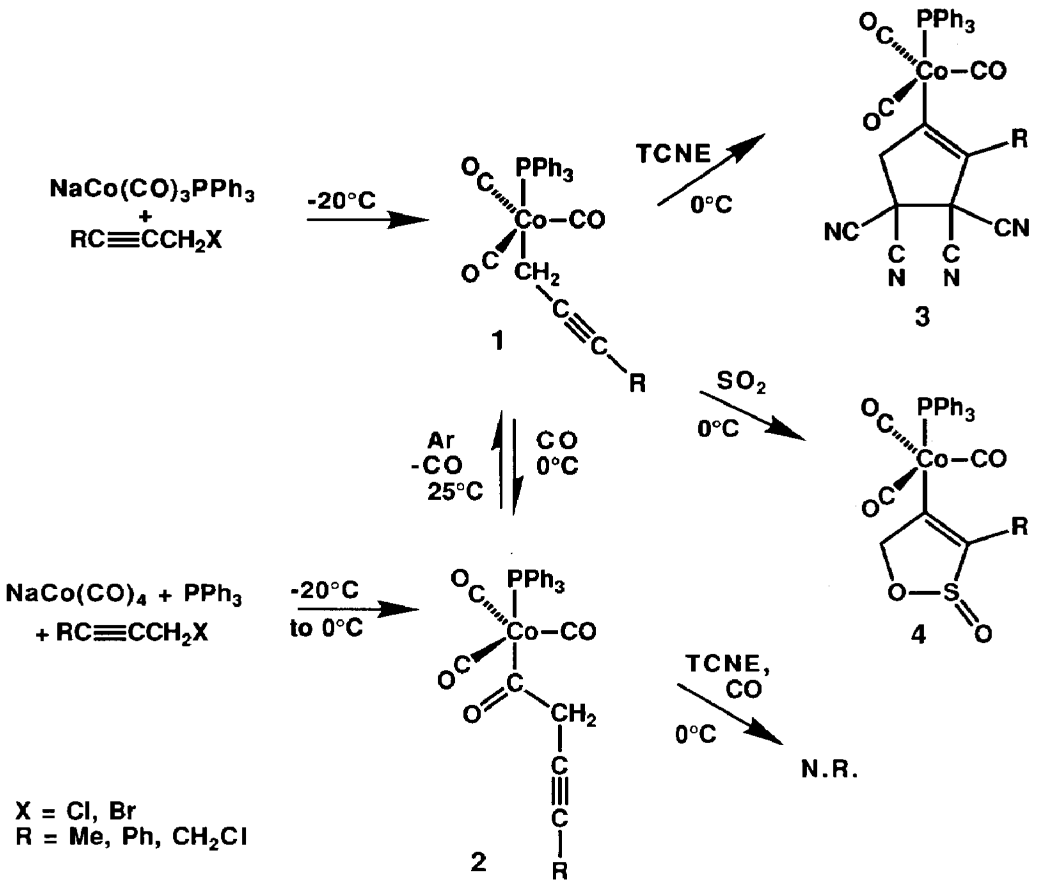
Similarly, reaction of equimolar amounts of **1b** and TCNE followed by workup, including chromatography, resulted in the isolation (33% yield) of $\overline{CH_2C(CN)_2(CN)_2C(Ph)=C}Co(CO)_3PPh_3$ (**3b**) as a light tan solid: FT IR (0.0472 *M*, THF (absorbance)) ν(CN) 2198 (0.01), ν(CO) 2055.4 (0.044), 1991.8 (0.597), 1978.8 (0.673) cm^{-1}; ^1H NMR (CD_2Cl_2 500.1 MHz) δ 7.59–7.30 (m, 4Ph), 3.97 (s, CH_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 196.94 (d, J(PC) = 23.63 Hz, 3CO), 155.13 (d, J(PC) = 27.86 Hz, =CCo), 135.07 (*C*Ph), 133.40–129.32 (4Ph), 112.25, 111.02 (4CN), 57.07 (d, J(PC) = 4.29 Hz, CH_2); $^{31}P\{^1H\}$ NMR (THF, 101.2 MHz) δ 54.57. Anal. Found: C, 66.37; H, 4.17; N, 7.97. $C_{36}H_{22}CoN_4O_3P$ calcd.: C, 66.67; H, 3.42; N, 8.63%.

Reaction of $MeC\equiv CCH_2Co(CO)_3PPh_3$ (1a) with SO_2

Sulfur dioxide gas was passed into a solution of **1a** (0.607 g, 1.32 mmol) in THF (16 ml) at 0 °C for 10 min. Volatile matter was removed in vacuo, and the residue was redissolved in 4 ml of THF to give a clear light brown solution. Chromatography of this solution on alumina at 0 °C eluting with diethyl ether afforded a light yellow band. This band was collected, and solvent was evaporated to leave 0.197 g (28% yield) of a pale yellow crystalline solid, $\overline{CH_2OS(O)C(Me)=C}Co(CO)_3PPh_3$ (**4a**): IR (THF) ν(CO) 2048 (vw), 1985 (vs), ν(C=C) 1604 (vw), ν(SO) 1127 (m), 1116 (m) cm^{-1}; ^1H NMR (CD_2Cl_2, 500.1 MHz) δ 7.5 (br, 3Ph), 5.60, 5.21 (br, CH_2), 2.22 (br, Me); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz) δ 197.6 (3CO), 143.32 (*C*Me), 142.58 (d, J(PC) = 23.90 Hz, CCo), 133.40–128.83 (3Ph), 90.41 (CH_2), 13.28 (Me); $^{31}P\{^1H\}$ NMR (THF, 101.2 MHz) δ 55.02. Anal. Found: C, 58.06; H, 4.00. $C_{25}H_{20}CoO_5PS$ calcd. C, 57.47; H, 3.86.

Results and discussion

Initial attempts at synthesis of cobalt-propargyl complexes were directed toward $RC\equiv CCH_2Co(CO)_4$ (R = Me or Ph). Infrared (IR) spectra of solutions containing $NaCo(CO)_4$ and $RC\equiv CCH_2X$ (X = Cl or Br) indicated that reaction had occurred; however, no organometallic products could be isolated from these mixtures. We then turned to the synthesis of $RC\equiv CCH_2Co(CO)_3PPh_3$, since analogous cobalt-alkyl tricarbonyl complexes display greater stability than the corresponding tetra-



Scheme 1

carbonyls [7–9]. The reactions conducted in this investigation are set out in Scheme 1.

Preparation and characterization of $RC \equiv CCH_2Co(CO)_3PPh_3$ (1)

Reaction of $NaCo(CO)_3PPh_3$ with $RC \equiv CCH_2X$ (R = Me, Ph, or CH_2Cl; X = Cl or Br) in THF under Ar at ca −20 °C followed by workup as described in Experimental afforded **1** as a white or yellow solid. When R = Me (**1a**) and Ph (**1b**), yields of 86 and 51%, respectively, were realized. However, when R = CH_2Cl (**1c**), the product is very soluble in organic solvents and only a 13% yield of very pure **1c** was obtained after crystallization from diethyl ether–pentane. The yield can be substantially increased by omitting crystallization and evaporating the solvent after chromatography. The products are stable to chromatography on alumina under Ar but decompose upon exposure to air, especially in solution.

The new cobalt-propargyl complexes were characterized by a combination of elemental analysis and IR and NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectroscopy. The IR spectra in the $\nu(CO)$ region show a weak band at 2038–2036 cm^{-1} and two strong bands between 1978 and 1960 cm^{-1}. This pattern is consistent with idealized C_{3v} symmetry of the trigonal bipyramidal tricarbonyl molecules (see Scheme 1) for which the degeneracy of the E mode is removed owing to axial perturbation. The spectra are similar to those reported for other $RCo(CO)_3PR'_3$ (R = alkyl or acyl; R' = alkyl, alkoxide, or related group) complexes [8,9], for which the inferred structures have been corroborated by X-ray cyrstallography in some cases [18–22].

The NMR spectra of **1** confirm the expected presence of a propargyl ligand. Thus, the proton spectra of **1a**,**1b** show the CH_2Co signal at the usual position [23–25]—δ 2.36 and 2.58, respectively—split by interaction with the phosphorus nucleus. In the $^{13}C\{^1H\}$ NMR spectra, resonances are observed for the different carbon atoms of the propargyl group, the equivalent CO's, and PPh_3. For example, the signal of the CO's appears at δ 201–200 as a doublet ($J(PC) = 18–20$ Hz), and that of the CH_2Co is seen at δ -4.85 to -7.81, also as a doublet ($J(PC) = 18–21$ Hz). The $^{31}P\{^1H\}$ NMR spectra of **1** attest to the absence of any other phosphorus-containing species.

Complexes **1** represent the first cobalt compounds that contain a propargyl ligand. In contrast, as mentioned in the Introduction, alkyl and related cobalt complexes of similar composition are numerous, and their chemistry has been well studied [7–9]. For many of these compounds, the corresponding acyl derivatives are also known and are sometimes accessible from the alkyls by carbon monoxide insertion. Therefore, it was of interest to determine whether isolable acylpropargyl complexes of cobalt could be obtained and whether they would be involved in equilibrium reactions with the propargyl complexes. We next describe our experiments directed at elucidating these points.

Preparation and characterization of $RC{\equiv}CCH_2C(O)Co(CO)_3PPh_3$ *(2)*

For the synthesis of complexes **2**, a suitable adaptation of the general method of Heck and Breslow [26] for $RC(O)Co(CO)_3PR'_3$ was employed. The method consisted of treating $NaCo(CO)_4$ in diethyl ether solution with one equivalent of each PPh_3 and $RC{\equiv}CCH_2X$, in the indicated order, under CO at -20 to 0°C. In this synthesis advantage is taken of the much greater reactivity of $RC{\equiv}CCH_2X$ toward $NaCo(CO)_4$ than toward PPh_3. Thus, $RC{\equiv}CCH_2Co(CO)_4$ forms initially and reacts with the already available PPh_3 to afford **2**. The acylpropargyl products are isolated as yellow solids by crystallization from diethyl ether–pentane. They are relatively unstable in solution, losing CO to give the corresponding complexes **1** (vide infra), and do not survive chromatography on alumina. When R = Me (**2a**) and Ph (**2b**), the products were obtained in very good yield (70%); however, when R = CH_2Cl (**2c**), the yield was again substantially reduced (14%) owing to very high solubility of the complex in organic solvents which precluded efficient crystallization.

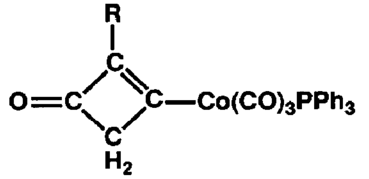
The acylpropargyl products **2** were characterized similarly to **1**. The IR spectra of **2** in the $\nu(CO)$ region are reminiscent of those of **1**, except that the bands are shifted to higher frequencies by up to 10 cm^{-1} and a medium-intensity $\nu(CO)$ absorption of the acyl group appears at 1669–1662 cm^{-1}. Thus, the structures of these complexes, like those of **1**, are trigonal bipyramidal with three equatorial CO's and axial PPh_3 and acylpropargyl. The presence of a $C(O)CH_2C{\equiv}CR$ ligand in **2** is also evident in the NMR spectra. For example, the proton resonance of the methylene group occurs at a lower field (δ 3.88–3.74) compared to its position (δ 2.58–2.36) in the spectrum of **1** and is not split by interaction with the phosphorus nucleus. The important resonances in the $^{13}C\{H\}$ NMR spectra are those of the acyl CO, which occur at δ 236.25 ($J(PC) = 35.33$ Hz) and 235.60 ($J(PC) = 36.36$ Hz) for **2a**,**2b**, respectively, and of the adjacent CH_2 (δ 52.22) which occur at lower fields compared to **1** (δ -7.2 and -7.8) and also experience splitting by the phosphorus nucleus ($J(PC) = 26.0$ and 26.5 Hz). The other features of the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **2** are those expected for the structures of these complexes.

The foregoing complexes are the first members of the transition-metal acylpropargyls. An attempt was made earlier to prepare a manganese-acylpropargyl complex by a CO insertion reaction, but the experiment proved unsuccessful [23]. In this study, the synthesis of **2** utilized PPh_3-assisted CO insertion into the propargyl carbon-to-cobalt bond of $RC{\equiv}CCH_2Co(CO)_4$. The successful outcome of this reaction suggested that the propargyl complexes **1** may also undergo a carbon monoxide insertion reaction, which would provide another synthetic method for **2**.

Carbonylation of $RC{\equiv}CCH_2Co(CO)_3PPh_3$ (1) and decarbonylation of $RC{\equiv}CCH_2C(O)Co(CO)_3PPh_3$ (2)

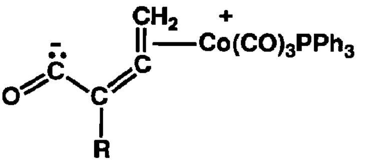
Exposure of solutions of the propargyl complexes **1a,1b** to 1 atm of CO at 0 °C for 24 (THF) or 90 h (CH_2Cl_2) results in the formation of the corresponding acylpropargyl complexes **2a,2b**. The reverse reaction, i.e. decarbonylation, can be effected by passing Ar through solutions of **2a,2b** in diethyl ether at room temperature for 1 h. The facile carbonylation–decarbonylation of **1a,1b**–**2a,2b** is reminiscent of the recently reported similar behavior of $ClCH_2Co(CO)_3PPh_3$–$ClCH_2C(O)Co(CO)_3PPh_3$, which also interconvert with ease [22]. In contrast, some related complexes, e.g., $MeCo(CO)_3PMePh_2$ and $MeOCH_2Co(CO)_3PMePh_2$ [27], easily add CO but the acyl products do not readily deinsert. Likewise, $RCo(CO)_3PR'_3$ complexes are known that do not insert CO at ambient conditions, but their acyl counterparts do decarbonylate [8,9]. The conversion of cobalt propargyls **1** to the acylpropargyls **2** in all probability involves $CH_2C{\equiv}CR$ migration onto one of the three equivalent CO's. Such a migratory insertion mechanism is suggested by the conversion of $PhCH_2Co(CO)_3PPh_3$ to $PhCH_2C(O)Co(CO)_2(^{13}CO)PPh_3$ with ^{13}CO [28] and by mechanistic studies on other metal–alkyl–acyl systems [29,30]. This pathway requires that the kinetic product of the insertion has the newly-formed acylpropargyl ligand in an equatorial position (C_s symmetry). A rapid rearrangement would then follow to the thermodynamically stable, isolable **2**, with the acylpropargyl and PPh_3 ligands in axial positions (C_{3v} symmetry). Since five-coordinate complexes display propensity for intramolecular rearrangements [31], the foregoing two-step pathway for the conversion of **1** to **2** appears entirely plausible.

It is of interest that reactions of **1** with CO yield the insertion products **2** rather than complexes derived by cycloaddition of CO to the propargyl ligand, I.



I

The formation of the latter needs to be considered, since CO is an unsaturated electrophilic molecule and as such might be expected to react similarly to SO_2, TCNE, $(CF_3)_2CO$, and $ClSO_2NCO$ to give cycloaddition products [1]. Notwithstanding this structural and electronic similarity, there is however a major mechanistic problem with such an addition of CO to $CH_2C{\equiv}CR$. This is because the developing negative charge in the resulting dipolar intermediate II would not be readily accommodated by the propargyl-appended CO; furthermore, this intermediate would be required to collapse to the relatively less stable four-membered cyclobutenone ring instead of the usual five-membered [3 + 2] cycloadduct.



II

Reactions of $RC{\equiv}CCH_2Co(CO)_3PPh_3$ (1) with TCNE and SO_2

Since CO was found to react with **1** by insertion into the Co–CH_2 bond, it appeared of interest to ascertain whether TCNE and SO_2 would also insert, or whether they would engage in [3 + 2] cycloaddition, as do other transition-metal-propargyl complexes [1]. In that vein, reactions were carried out between **1a**,**1b** and TCNE and resulted in the isolation of white (**3a**) and tan (**3b**) solids whose elemental analysis and spectroscopic data are consistent with the formulations as [3 + 2] cycloadducts. Similarly, treatment of **1a** in THF with gaseous SO_2 yields the yellow sultine complex **4a**. The IR spectra in the ν(CO) region of **3a**,**3b** and **4a** point to their C_{3v} molecular symmetry, and the ^1H and $^{13}C\{^1H\}$ NMR spectra closely resemble those of the corresponding compounds of other metals [23,24,32,33]. The synthesis of these cycloaddition products shows that **1** will react either at the Co–CH_2 bond (CO insertion) or at the $C{\equiv}C$ bond (cycloaddition) depending on the nature of the adding species. In contrast to **1a**,**1b**, the acylpropargyl complex **2a** did not react with TCNE in THF under CO at 0 ° C for 36 h. This behavior is consistent with the generally accepted mechanism of [3 + 2] cycloaddition reactions of metal-propargyl complexes [1,3], since the acylpropargyls cannot react by a similar low energy path.

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