Deprotonation of Hexacarbonyl(trimethylsilylethyne)dicobalt and Subsequent Single Electron Transfer Chemistry. Polyacetylene–Poly(cobaltcarbonyl) Complexes

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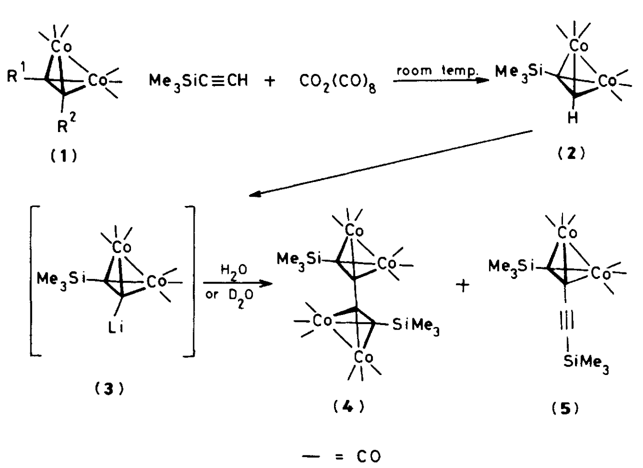
Deprotonation of hexacarbonyl(trimethylsilylethyne)dicobalt with $LiN(SiMe_3)_2$ gave the lithium species (**3**), which on treatment with a variety of electrophiles, gave products characteristic of single electron transfer chemistry.

The readily prepared air-stable complexes of $Co_2(CO)_8$ and alkynes, (**1**), are finding increasing use in organic synthesis.[1] While examining the chemistry of alkyne–$Co_2(CO)_6$ complexes, we have studied the deprotonation of the red crystalline air-stable adduct (**2**),[2] in order to compare and contrast the chemistry of lithium acetylide with the $Co_2(CO)_6$ complex (**3**).[3] It was found that treatment of (**2**) in Et_2O at −78 °C with either $LiNPr^i_2$ or $LiN(SiMe_3)_2$, followed by



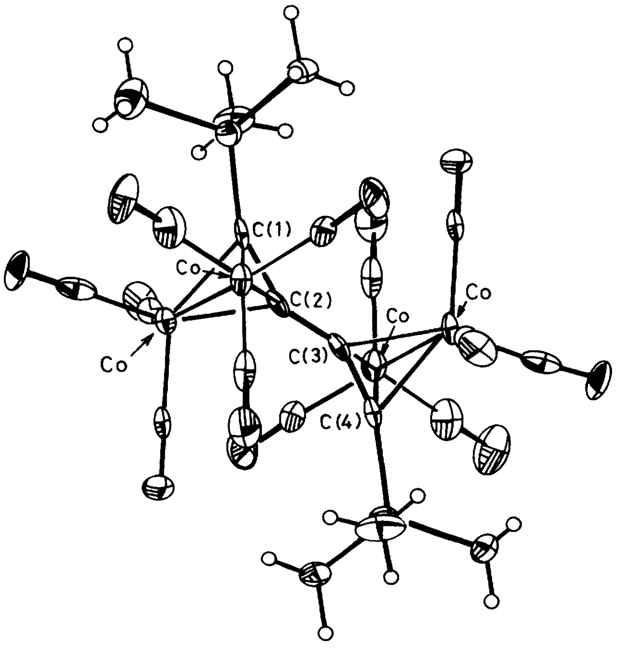
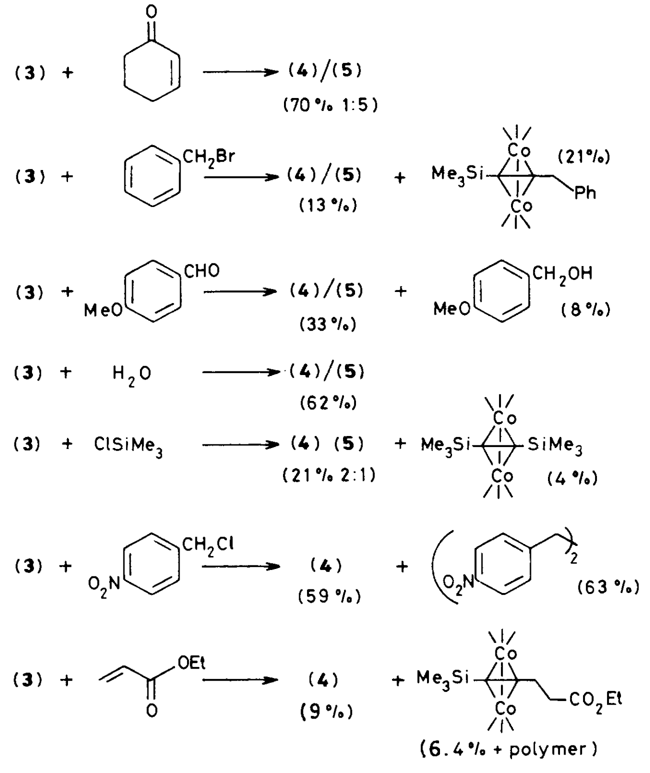
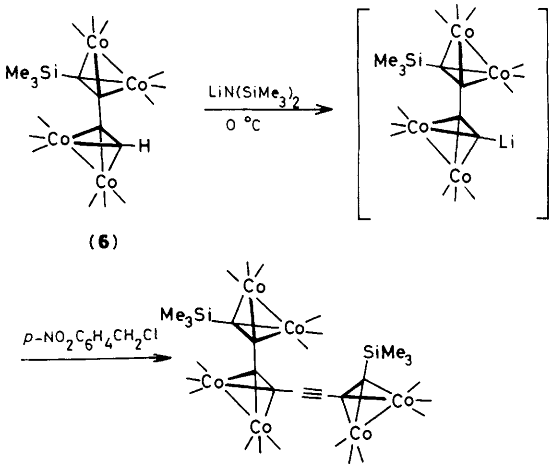


Figure 1. The crystal structure of (**4**).

warming to *ca.* 0 °C, gave dark green–black solutions of a species that we have formally written as the simple lithio-compound (**3**). In view of the recent single crystal *X*-ray stuctures, and theoretical calculations on the structures of organolithium compounds, it is reasonable to assume that (**3**) is in reality substantially different (dimeric Li bridging *etc.*), probably with significant charge delocalization onto the Co atoms.[4] The cyclic voltammetry of (**3**) gave an irreversible wave up to 50 V s^{-1} (an approximate oxidation potential of +0.58 V *vs.* a standard calomel electrode at a scan rate of 1000 mV s^{-1} in tetrahydrofuran, THF, at −55 °C was observed), suggesting rapid electron transfer to give a new species that cannot reverse. When solutions of (**3**) were quenched with H_2O or D_2O only the dimers (**4**) and (**5**) (62%) (1 : 1) were formed. Decomplexation of (**4**) and (**5**) using *N*-methylmorpholine *N*-oxide, (much milder than the conventional Ce^{IV} oxidation which tended to decompose the alkynes, gave 1,4-bis(trimethylsilyl)buta-1,3-diyne.[5,6] The dimer (**4**) is a dark green crystalline compound, m.p. 180 °C (decomp.),[7]



Scheme 1



(**6**)

(**7**)

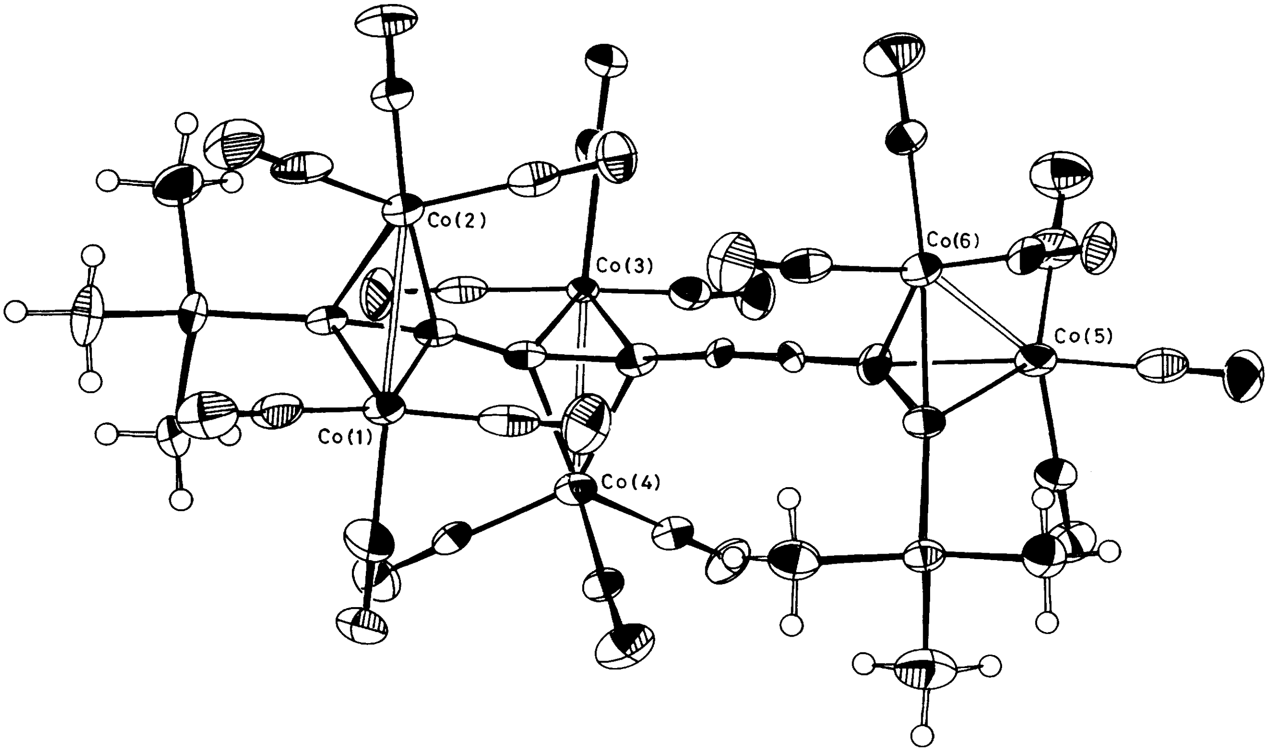
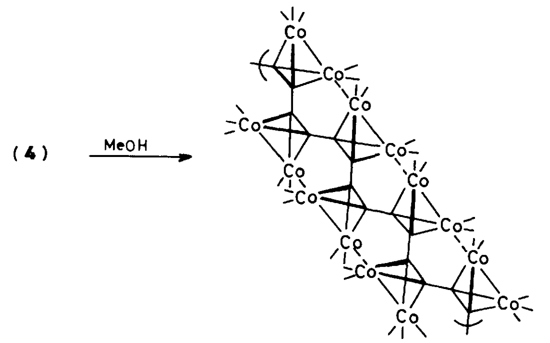


Figure 2. The crystal structure of (**7**).



(8)

whereas (5) is a red oil. That (4) is green suggested that there must be some conjugation between the two cobalt-capped alkyne groups. The single crystal *X*-ray structure of (4) (Figure 1) shows no horizontal Co interactions across the C(2)–C(3) bond, but the C(1)–C(2)–C(3) angle of 146.8°, and the C(2)–C(3) bond length, 1.43 Å, indicate that the central bond has substantial double bond character.†

When the deprotonation of (2) was carried out in an n.m.r. tube it was shown that the dimers (4) and (5) were not formed until H_2O was added, therefore excluding a disproportionation pathway from (3) to (4)/(5). When solutions of (3) were treated with electrophiles, as shown in Scheme 1, the dimers (4) and (5) were formed in the amounts indicated, along with products indicative of a single electron transfer mechanism operating.[9]

To extend further the proposition that dimerization of alkyne–cobalt complexes can be achieved by deprotonation and subsequent electron transfer to an electrophile, we prepared the complex (6).‡ Deprotonation of (6) using the same conditions as for (3), followed by quenching with 4-nitrobenzyl chloride, gave the complex (7), (6%). An authentic sample of this complex was prepared by treating 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne[6] with a large excess of $Co_2(CO)_8$. The complex (7) was identical to the material prepared *via* the dimerization route. We could not find conditions that allowed complete complexation of the tetrayne to the octacobalt complex. The single crystal *X*-ray structure of (7) (Figure 2)† shows two adjacent cobalt–alkyne units, an isolated alkyne followed by another cobalt–alkyne unit. It clearly shows that the isolated alkyne is too hindered to allow cobalt complexation.

Finally, when the bis(trimethylsilyl) dimer (4) was allowed to stand in MeOH, a black insoluble polymer slowly (24 h) precipitated. The microanalytical data and C/Co ratio indicated it to be a polyacetylene (*ca.* 30 units), with each triple bond capped by a $Co_2(CO)_6$ unit.§ There may be some gaps, by analogy with the structure of (7) but at present this is not known. Formally, we can represent the structure of this material as (8).

The potential for (4), (7), and (8) to act as 'molecular metals' is apparent, since they are low-dimensional solids containing low-valent metal clusters and can function as electron reservoirs.[10] Preliminary experiments have indicated that (4) and (8) exhibit electrical conductivity.

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† *Crystal data:* (4) $Co_4Si_3O_{12}C_{22}H_{18}$, $M = 760.23$, monoclinic, space group *C2/c*, $a = 15.683(7)$, $b = 8.991(3)$, $c = 21.819(9)$ Å, $\beta = 100.98(2)°$, $U = 3020.23$ Å^3, $D_c = 1.672$ g cm^{-3} for $Z = 4$ (at -160 °C), $\lambda = 0.71069$ Å, μ(Mo-K_α) = 22.878 cm^{-1}. A total of 1747 observed data (out of 1982 unique for $6° < 2\theta < 45°$) refined to $R(F) = 0.041$ and $R_w(F) = 0.035$. The diffractometer, data reduction techniques, *etc.*, have been described previously in ref. 8.

Compound (7) $Co_6C_{32}H_{18}O_{18}Si_2$, $M = 1100.25$, triclinic, space group $P\bar{1}$, $a = 15.458(3)$, $b = 14.231(3)$, $c = 9.751(2)$ Å, $\alpha = 101.49(1)$, $\beta = 88.62(1)$, $\gamma = 88.39(1)°$, $U = 2100.27$ Å^3, $D_c = 1.740$ g cm^{-3} for $Z = 2$ (at -159 °C), $\lambda = 0.71069$ Å, μ(Mo-K_α) = 24.374 cm^{-1}. A total of 4481 observed data (out of 5524 unique) refined to $R(F) = 0.041$ and $R_w(F) = 0.042$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The crystalline complex (6) was prepared by treating 1-trimethylsilylbuta-1,3-diyne with excess $Co_2(CO)_8$ in hexane.

§ For a repeating two-carbon–two-cobalt unit, each with six CO ligands, *i.e.* $(Co_2C_8O_6)_n$, Co = 38.03; C = 30.97%. The polyacetyline adduct (8) gave Co = 37.90; C = 30.48%. I.r. (Nujol) 2095, 2077, 2058, 2020, and 2001 cm^{-1}.