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Synthesis and structural characterisation of the acetylene-linked dimeric cluster $[\{Co_2(CO)_6PhC_2\}_2]$

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Abstract

An acetylene-linked dimeric complex has been prepared from the reaction of $[Co_2(CO)_8]$ with PhC_2MPPh_3 (M = Ag or Au) or $[Hg(C_2Ph)_2]$ in CH_2Cl_2. An X-ray structure determination revealed that the product was not the expected acetylene derivative $[Co_2(CO)_6(PhC_2MPPh_3)]$ or $[\{Co_2(CO)_6PhC_2\}_2Hg)]$, but contained two $[Co_2(CO)_6PhC_2]$ units linked by a C–C bond to give the dimer $[\{Co_2(CO)_6PhC_2\}_2]$.

We are currently interested in the chemistry of polymeric materials which contain clusters supported on a carbon backbone. There have been a number of reports of cobalt-based clusters in polymeric materials. Patin et al. [1] reported the synthesis of the monomer $[RCCo_3(CO)_9]$ (R = 1,4-$C_6H_4CH{=}CH_2$) which undergoes free radical copolymerisation with styrene or methyl acrylate to produce new polymeric materials [2]. Seyferth et al. [3] have also prepared several polymerizable monomers of a similar type although no experimental details are available regarding their polymerization. Polymers containing the $[Co_2(CO)_6C_2]$ unit are known [3,4]. Most importantly, Magnus and Becker [4] have reported the synthesis of the dimers $[\{Co_2(CO)_6(Me_3SiC_2)\}_2]$ and $[\{Co_2(CO)_6\}_2(Me_3SiC_2C_2H)]$. These contain two linked $[Co_2(CO)_6C_2]$ units and are relevant to the work discussed here. More recently, the compounds $[Co_2(CO)_6(RC_2H)]$ have been reported [5] to undergo oxidative-coupling to generate a trimer; a hexacobalt complex of cyclo[18]carbon and dimer $[\{Co_2(CO)_4(dppm)(Me_3SiC_2C_2)\}_2]$. Here we wish to report the synthesis and full characterisation of the dimer $[\{Co_2(CO)_6PhC_2\}_2]$, **1**.

On reaction of dicobalt octacarbonyl, $[Co_2(CO)_8]$, with PhC_2MPPh_3 (M = Ag or Au or $[Hg(C_2Ph)_2]$, in CH_2Cl_2, the initial brown solution turns first to red and then to green. After separation by TLC using hexane/THF as eluant two compounds are obtained. The first red-brown solid is formed in very low yield and it has not been possible to fully characterise this compound. However, on the basis of its IR spectrum (ν(CO) 2094 (m), 2081 (w), 2062 (vs), 2037 (vs), 2032 (vs, sh), 1988 (w, br) cm^{-1}) which is similar to $[Co_2(CO)_6(PhC_2H)]$, we tentatively formulate this compound as $[Co_2(CO)_6(PhC_2MPPh_3)]$. The major product, which is the same irrespec-

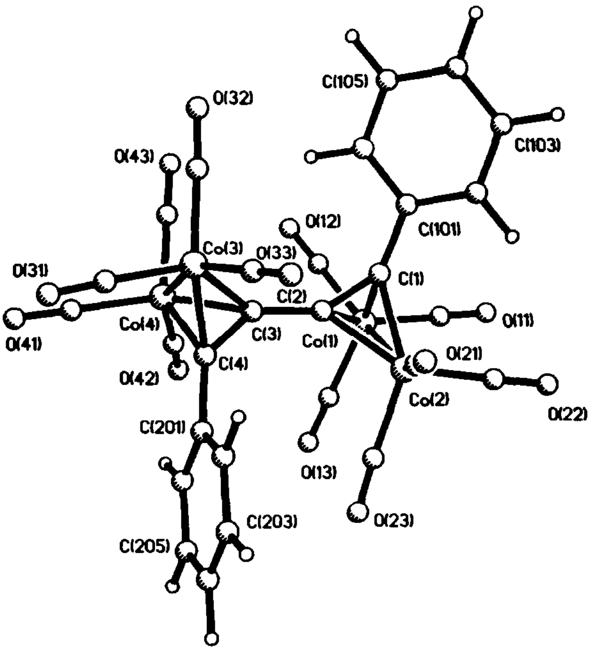

Fig. 1. The molecular structure of [{$Co_2(CO)_6PhC_2$}$_2$] showing the atom labelling. Bond lengths: Co(1)–Co(2), 2.461(1); Co(3)–Co(4), 2.461(1); Co(1)–C(1), 1.976(6); Co(1)–C(2), 1.979(6); Co(2)–C(1), 1.956(6); Co(2)–C(2), 1.984(6); C(1)–C(2), 1.336(8); Co(3)–C(3), 1.993(6); Co(3)–C(4), 1.953(6); Co(4)–C(3), 1.981(6); Co(4)–C(4), 1.966(6); C(3)–C(4), 1.331(8) Å. Bond angles: C(2)–C(1)–C(101), 140.8(6); C(3)–C(4)–C(201), 137.6(6); C(1)–C(2)–C(3), 144.6(6); C(2)–C(3)–C(4), 138.9(6)°.

tive of whether PhC_2MPPh_3 or [Hg($C_2Ph)_2$], is employed, is green. The EI mass spectrum of the green component shows a parent ion at $m/z = 774$ amu and has a fragmentation pattern which shows the loss of twelve carbonyl ligands. This mass spectrum together with the microanalytical data shows the stoicheiometry to be $Co_2C_{14}H_5O_6$ corresponding to the formulation [{$Co_2(CO)_6PhC_2$}$_2$] (rrm 773.4). The new cluster exhibits IR carbonyl absorptions at 2101 (m), 2082 (s), 2062 (vs), 2037 (s), 2028 (s, sh), 1984 (w, br) cm^{-1}. These are very similar to those observed [6] for other related species such as [$Co_2(CO)_6(PhC_2H)$] and [$Co_2(CO)_6(PhC_2Ph)$]. The ^1H NMR spectrum of **1** in C_6D_{12} (250 MHz, 20 °C) shows two broad peaks in the aromatic region, centred at ca. δ 7.5 (2H) and 7.2 (3H) ppm, which confirm the presence of the CPh unit. The $^{13}C\{^1H\}$ NMR spectrum of **1** (in $CDCl_3$, 100.6 MHz, 20 °C) is well resolved and exhibits seven signals at δ 93.03, 99.28, 127.93, 128.66, 129.28, 138.35, and 198.79 ppm. This spectrum has features in common with the spectra found for the other cobalt-diyne complexes discussed above. A comparison of the $^{13}C\{^1H\}$ NMR spectrum of **1** with that of [$Co_2(CO)_6(PhC_2Ph)$] [7] reveals marked similarities in the aromatic region. Further comparison of the $^{13}C\{^1H\}$ NMR spectrum of **1** with that recorded for the complex [{$Co_2(CO)_6$}$_2$($HC_2C_6H_4C_6H_4C_2H$)] allowed us to the assign the signal at δ 93.03 ppm to the carbon atom C(1) (see Fig. 1) attached to the phenyl ring since the chemical shift is close to the resonance attributed to the similar proton in [{$Co_2(CO)_6$}$_2$($HC_2C_6H_4C_6H_4C_2H$)]. The remaining signal at δ 99.28 ppm is therefore due to the "alkyne" carbon atom joined to the {$Co_2(CO)_6C_2$} moiety. The low field resonance at δ 199.79 ppm may be assigned to the two equivalent sets of carbonyl ligands which at this temperature are clearly undergoing fluxional processes.

In order to confirm the spectroscopic assignments a single-crystal X-ray structure determination was undertaken. Suitable dark green platelets were obtained from hexane at 0 °C. The molecular structure of $[\{Co_2(CO)_6PhC_2\}_2]$, together with selected bond parameters is shown in Fig. 1 *. The overall structure resembles that of $[\{Co_2(CO)_6Me_3SiC_2\}_2]$ [4], with the two $\{Co_2(CO)_6C_2\}$ units linked through an "alkyne" carbon atom, and the "alkyne" C≡C vectors lying perpendicular ot the Co–Co vectors. The two independent Co–Co bond lengths are equal (2.461(1) Å), and are similar in length to the average value of 2.474 Å found in $[\{Co_2(CO)_6Me_3SiC_2\}_2]$ [4]. Although the estimated standard deviations on the Co–C(alkyne) bond lengths are rather high to make detailed comments, the Co–C lengths within the quasi-tetrahedra can be divided into two groups, with "long" and "short" interactions. The Co–C distances involving the two linked carbons, C(2) and C(3) (average 1.96 Å), are ca. 0.02 Å shorter than the distances involving C(1) and C(4) (average 1.98 Å). This tilting of the C–C vector with respect to the Co–Co vector presumably reflects the difference in the nature of the substituents on the "alkyne" carbons. In the related alkyne complexes $[Co_2(CO)_6(PhC_2Ph)]$ and $[Co_2(CO)_6({}^tBuC_2{}^tBu)]$ [7], where the substituent groups are the same, in each complex, no such tilting is observed. The central carbon–carbon bond observed in $[\{Co_2(CO)_6PhC_2\}_2]$ (C(2)–C(3) 1.430(8) Å) is significantly longer than the "alkyne" carbon–carbon bonds, C(1)–C(2) (1.336(8) Å) and C(3)–C(4) (1.331(8) Å), which are equal to within experimental error. This central carbon–carbon bond distance shows reasonable agreement with the corresponding bond length in $[\{Co_2(CO)_6Me_3SiC_2\}_2]$ of 1.432 Å [4]. Although longer than the "alkyne" bonds, the central carbon–carbon bond is significantly shorter than expected for a single carbon–carbon bond. This suggests that delocalisation of the electron density from the "alkyne" bonds along the carbon backbone of the molecule has occurred. The carbon–carbon "alkyne" bonds show a lengthening from the distances anticipated for a C≡C bond, in a free alkyne (1.18 Å) [8], which is entirely consistent with delocalisation of electron density into the Co_2 units and into the C–C linking bond. The C(1)–C(2)–C(3) and C(2)–C(3)–C(4) bond angles of 144.6(6)° and 138.9(6)°, respectively, have been greatly reduced from the 180° seen in alkynes, but are similar to the equivalent angle of 146.7° observed in $[\{Co_2(CO)_6Me_3SiC_2\}_2]$ [4].

These studies suggest that the formation of complexes of the type $[Co_2(CO)_6(PhC_2MPPh_3)]$ appears to occur in the initial stages of the reactions of PhC≡CMPPh$_3$ with $[Co_2(CO)_8]$ (M = Au or Ag) as indicated by the initial formation of a red solution, the IR of which compared favourably to those of the

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* 1: $C_{28}H_{10}O_{12}Co_4$, M 773.4, monoclinic, space group $P2_1/n$ (alt. setting $P2_1/c$, No. 14), a 8.962(1), b 17.714(1), c 18.575(2) Å, β 90.61(1)°, V 2949 Å^3, $Z = 4$, D_c 1.743 g cm^{-3}, $F(000) = 1528$, $\mu(\text{Mo-}K_\alpha) = 0.64$ cm^{-1}. 4419 reflections measured on a Stoe four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ 0.71069 Å), and $2\theta_{max}$ 45°, 3524 unique data ($R_{int} = 0.025$), and 2902 observed with $F > 4\sigma(F)$. Structure solved by direct methods (Co atoms) and Fourier difference techniques, and refined by blocked full-matrix least-squares (all non-hydrogen atoms anisotropic) to $R = 0.053$ and $R_w = 0.051$; hydrogen atoms placed in fixed positions riding on relevant C atoms. Details of atomic coordinates, thermal parameters, bond parameters and structure factors may be obtained from the authors.

complexes, $[Co_2(CO)_6(RC_2R')]$. However, these species are not stable and quickly lose the bulky $AuPPh_3$ group to generate the complex $[\{Co_2(CO)_6(PhC_2)\}_2]$ in a manner similar observed in the formation of $[\{Co_2(CO)_6(Me_3SiC_2)\}_2]$ from $[Co_2(CO)_6(Me_3SiC_2)]Li$ [4]. A red dimer of the same formulation has previously been described [9] as the product of the reaction of $[Co_2(CO)_8]$ with PhC_2SnMe_3. We have repeated this earlier reaction [10] and believe the product to be the red complex, $[Co_2(CO)_6PhC_2SnMe_3]$.

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