Nuclear Recoil Synthesis of Metallorganic Compounds and Crystal Structure of $Co_3(CO)_9(C_6H_7)$

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Abstract

The formation of the complexes $Co_2(CO)_6(C_6H_8)$ (I) and $Co_3(CO)_9(C_6H_7)$ (II) by nuclear recoil of ^{60}Co and T is reported together with the crystal structure of **II**. The very low T activity found in **II** suggests that benzvalene species play an important role in the formation of **II**. The crystal structure of **II** has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, a = 8.593(4), b = 14.305(7), c = 8.144(5) Å, α = 95.28(2), β = 112.24(2), γ = 100.78(2)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares to R = 0.0578 for 1456 observed reflections. The structure consists of an equilateral triangular cluster of Co atoms [Co–Co bond distances: 2.450(3), 2.451(3) and 2.459(3) Å]. A carbon atom from the (2-cyclopenten-1-methylidine) ligand nearly symmetrically caps the metal triangle [Co–C bonds: 1.883(11), 1.901(11) and 1.902(14) Å].

Introduction

The formation of $Co_2(CO)_6(C_6H_8)$ (I) and $Co_3(CO)_9(C_6H_7)$ (II) has been previously reported [1]. Owing to the theoretical and practical significance of the shrinking of six-membered to five-membered rings the crystal structure of **II** and a tracer study on the formation of both **I** and **II** are reported. In the attempt to investigate the nature of the reaction intermediates, the nuclear recoil technique has been used to label both the organic and the inorganic moieties of the complexes. The nuclear recoil technique produces intermediate labelled species which are similar in nature to the species obtained by radiolysis, though in extremely lower yield, so that the main difference between the radiolytical and the nuclear method is the significant lower radiation dose delivered to the sample.

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Experimental

The radiation synthesis of the above complexes has been reported elsewhere [1]. Crystals of **II** for the X-ray diffraction study were obtained by recrystallization at 253 K from tetrahydrofuran. For tracer studies 4.5 ml of a 1.9×10^{-2} molar solution of $Co_2(CO)_8$ in benzene and 0.10 ml of a 2 molar solution of C_6H_5Li in benzene/ether (70/30%, Fluka) were sealed under vacuum in a quartz bulb. The sample, contained in an aluminium cylinder, was irradiated for one hour in the pool of Triga Mark II reactor of the University of Pavia.

After the neutron bombardment and the addition of a carrier solution prepared by γ-radiolysis [1], the mixture was purified by TLC [1] and each product, dissolved in 20 ml of Insta-Gel liquid scintillation cocktail, was measured for its β^- activity (T + ^{60}Co) by means of a Tri-Carb 2200 CA (Packard) liquid scintillation counter, the Tri-Carb 2200 CA computer program was used to resolve the T β^- activity from the β^- activity of ^{60}Co. The ^{60}Co γ activity was also measured by γ spectrometry using a NaI (Tl) crystal.

Crystal Structure Determination of the Complex $Co_3(CO)_9(C_6H_7)$ (II)

A flattened crystal of approximate dimensions 0.08 × 0.25 × 0.45 mm was used for the X-ray data collection. Unit-cell parameters were obtained by least-squares refinement of the θ values of 25 carefully centred reflections (with θ in the range 10–15°).

Crystal data

$C_{15}H_7Co_3O_9$, M = 508.01, triclinic, space group $P\bar{1}$, a = 8.593(4), b = 14.305(7), c = 8.144(5) Å, α = 95.28(2), β = 112.24(2), γ = 100.78(2)°, V = 910.3(7) Å^3, Z = 2, D_c = 1.853 g cm^{-3}, $F(000)$ = 500, μ(Mo Kα) = 27.42 cm^{-1}.

Data were collected at room temperature on a Siemens AED diffractometer using niobium-filtered

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Mo Kα radiation ($\bar{\lambda}$ = 0.71069 Å) and the $\theta/2\theta$ scan technique, the individual profiles having been analyzed according to Lehmann and Larsen [2]. All reflections with θ in the range 3–24° were measured. Of 2811 independent reflections, 1456, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. No correction for absorption effects was applied. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares, first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed at their geometrically calculated positions (C–H = 1.0 Å) and introduced in the final structure factors calculations with fixed isotropic thermal parameters. The SHELX system of computer programs was used [3]. In the last cycles of refinement a weighting scheme was used, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, with K = 0.569 and g = 0.032. The final atomic coordinates for the non-hydrogen atoms are given in Table 1. Final R and R' values were 0.0578 and 0.0609, respectively. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 4. All calculations were performed on the GOULD POWERNODE 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. See also 'Supplementary Material'.

TABLE 1. Fractional atomic coordinates (×10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of the complex $Co_3(CO)_9(C_6H_7)$

Atom	x/a	y/b	z/c
Co(1)	5150(2)	2704(1)	2707(2)
Co(2)	8180(2)	2865(1)	829(2)
Co(3)	7300(2)	3488(1)	3904(2)
O(1)	2327(14)	2268(8)	5999(15)
O(2)	3871(17)	1203(10)	704(19)
O(3)	4318(13)	4419(9)	1684(15)
O(4)	7921(19)	1365(10)	−1755(17)
O(5)	8497(14)	4584(9)	−1041(17)
O(6)	11717(13)	2835(11)	269(15)
O(7)	5356(15)	3109(10)	7597(14)
O(8)	10528(14)	3736(9)	4371(16)
O(9)	7157(15)	5458(8)	3333(16)
C(1)	3442(15)	2452(10)	4720(19)
C(2)	4427(19)	1802(10)	1437(21)
C(3)	4635(15)	3769(11)	2035(17)
C(4)	8038(19)	1960(11)	−760(20)
C(5)	8379(16)	3945(12)	−323(16)
C(6)	10347(19)	2863(12)	525(18)
C(7)	6039(17)	3288(10)	6181(18)
C(8)	9280(17)	3626(10)	4164(16)
C(9)	7201(16)	4712(11)	3583(18)
C(10)	6961(14)	2229(8)	2981(14)
C(11)	6956(18)	1299(9)	3690(18)
C(12)	6620(23)	447(11)	2609(24)
C(13)	7787(34)	−126(15)	2345(30)
C(14)	9022(33)	280(17)	3149(37)
C(15)	8698(23)	1221(11)	3781(25)

Results and Discussion

After neutron bombardment the radioactive solution does not show any macroscopic change and is slightly lighter than the corresponding solution after radiolysis at 8.10^5 Gy. The dose absorbed by the sample during neutron bombardment is very low (~ 5 kGy), so none of the compounds of interest can be observed on the TLC plates without the addition of a carrier solution prepared by γ-radiolysis [5]. Four compounds have been carefully isolated and analyzed for their activities: $Co_2(CO)_6(C_2H_2)$, $Co_2(CO)_6(C_6H_8)$ (I), $Co_3(CO)_9(C_6H_7)$ (II) and $Co_4(CO)_{12}$. Only a very small fraction of the total produced activities of both ^{60}Co and T have been observed in the complexes. Namely: 0.02% of ^{60}Co and only trace of T in $Co_2(CO)_6(C_2H_2)$; 0.03% of ^{60}Co and 0.1% of T in I; 0.1% of ^{60}Co and 0.4% of T in II; 0.3% of ^{60}Co in $Co_4(CO)_{12}$. The bulk of the ^{60}Co activity was detected as insoluble brown material at the start band of the TLC plates, whereas T was mainly distributed between liquid benzene and solid polymeric organic compounds such as diphenyl and phenylcyclohexadiene [1, 5–9], which are eluted as undifferentiated broad bands between II and $Co_4(CO)_{12}$.

Typical activities for I are: ^{60}Co = 136 dpm, T = 870 dpm, Co:T ratio 1:6.4 and for II: ^{60}Co = 565 dpm, T = 3775 dpm, Co:T ratio 1:6.7. All counting data are the average of at least four different experiments.

Owing the large difference in the radiation doses absorbed by the samples, the yields of the complexes differ significantly from those previously reported [1].

Natural lithium contains 7.42% of ^6Li which under thermal neutron bombardment yields tritium accordingly to the ^6Li (n, α) T reaction. The recoil energy of the T species is 2.06 MeV which is very suitable for recoil labelling in the condensed phase [10]. Recoil T reactions in liquid benzene have been widely studied in the past [5–9] and the role of 1,3- and 1,4-cyclohexadienyl-T radicals has been pointed out [8] as precursors of both labelled polymeric organic materials and 1,3-, 1,4-cyclohexadienes which are produced in about 3 and 4% yields, respectively [8, 9].

The (n, γ) reaction on ^{59}Co (100%) yields ^{60}Co with a maximum recoil energy of about 500 eV. The recoil energy spectrum for the $^{59}Co(n,\gamma)^{60}Co$ reaction has been reported [11a] and on the basis of the available bond energy data for $Co_2(CO)_8$ [11b] it can be predicted that almost every ^{60}Co leaves its original molecule upon recoil. The appearance of ^{60}Co containing complexes is consistent with the observation that, in hydrocarbon solution, at about the same concentration with yields from 10 to 30% for maximum recoil energies ranging from 903 to 86 eV, recombination of metal carbonyls occurs [12] so that the ^{60}Co activity in all the observed complexes comes from random distribution of ^{60}Co in the recombined metal carbonyls and in their radiolysis products [13–15] whereas the tritium activity comes from recoil labelling of the precursor of the organic moiety of the complex. The tritium activity recovered in $Co_2(CO)_6(C_2H_2)$ is negligible being the organic moiety of the complex formed by γ-radiolysis of the solvent.

It has been already reported [1, 16–18] that metal carbonyls may act both as radical scavengers and energy sinks for highly excited species. The cyclohexadienyl radicals formed by the reaction of recoil T with benzene may follow three reaction paths: (a) reaction with the solvent to polymeric organic material; (b) reaction with the solvent (T addition) to give excited cyclohexadiene which further reacts with the carbonyl to form complex **I**; (c) reaction with already formed polynuclear carbonyl species [13–15] accompanied by isomerization to 2-cyclopentene-1-methylidene species. Isomerization to C_5 rings has been already observed for cyclo-C_6 excited species both by UV light [19] and nuclear decay [20].

Reaction paths (b) and (c) have already been proposed for the formation of complexes **I** and **II** by radiolysis [1]. Now the study of the labels distribution into the two molecules, i.e. T:^{60}Co ratio 6.4:1 in complex **I** and 6.7:1 in complex **II**, clearly indicates that the effective cause of the formation of the metal carbonyl complexes is the formation of the organic radical ligands which then react with carbonyl species. The very low yield of the T-labelled complex **II** versus the labelled cyclohexadiene-T in liquid phase recoil experiments [8, 9], suggests an alternative route for the formation of the complex **II**. Gas phase radiolysis of benzene derivatives yields benzvalene [21, 22], the valence isomer of benzene with the lowest energy content [23]. Benzvalene has never been isolated from liquid benzene radiolysis or photolysis. It has been suggested that rapid collisional quenching of excited states prevents conversion to the isomer in the condensed phase, at least for photolysis [21]. Nevertheless, by laser flash photolysis of benzene in aerated water solution, benzvalene was observed as a transient and the formation of cyclopentadienaldehyde, which was detected as final product by UV absorption spectroscopy, was attributed to the reaction of the transient with water or oxygen [24]. In hot atom chemistry experiments, the formation of benzvalene-T or its derivatives have never been observed probably for the reason given before. In our experiment, the presence of the carbonyl species acting as stabilizers and energy sink for excited species, suggests the presence of a further reaction path: the reaction of recoil T with benzvalene transient leading to a 2-cyclopentene-1-methylidene radical which is stabilized by the carbonyl fragment. This reaction path

$$\text{benzene} \xrightarrow{\gamma} \text{benzvalene} \xrightarrow{T^*} {}^{\bullet}C_6H_6T^* \longrightarrow \text{complex } \mathbf{II}$$

seems to be in good agreement with both the principle of the last motion [25] and the low yield of **II**. The role of cationic species, though possibly effective, has not been investigated so far.

Description of the Crystal Structure of $Co_3(CO)_9(C_6H_7)$ (II)

The structure of **II** is represented in Fig. 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table 2. The structure consists of an equilateral triangular cluser of Co atoms [Co–Co bond distances: 2.450(3), 2.451(3) and 2.459(3) Å] each of which is bonded to three terminal carbonyl groups. By considering the C(10) carbon atom from the (2-cyclopentene-1-methylidine) ligand nearly symmetrically capping the metal triangle [Co–C(10) bonds: 1.883(11), 1.901(11) and 1.902(14) Å], a distorted tetrahedral Co_3C 'core' can be envisaged. Of the three carbonyl groups bonded to each Co atom, two can be classified as equatorial and one

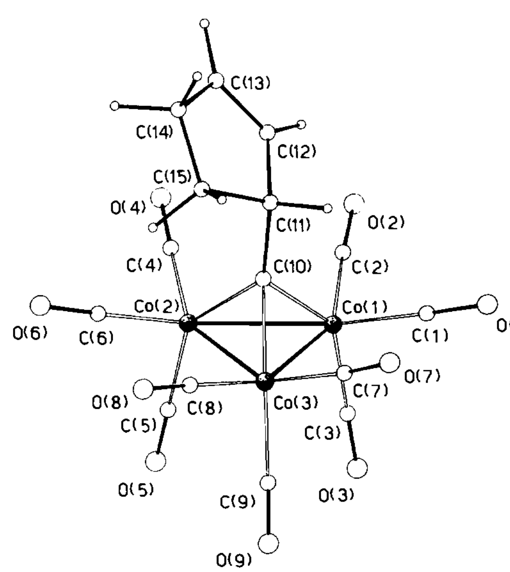

Fig. 1. View of the structure of the complex $Co_3(CO)_9$-(C_6H_7) (II).

TABLE 2. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses in complex **II**

Co(1)–Co(2)	2.450(2)	Co(1)–Co(3)	2.451(3)
Co(2)–Co(3)	2.459(3)	Co(1)–C(1)	1.751(12)
Co(1)–C(2)	1.749(16)	Co(1)–C(3)	1.845(17)
Co(2)–C(4)	1.766(16)	Co(2)–C(5)	1.828(17)
Co(2)–C(6)	1.784(17)	Co(3)–C(7)	1.777(13)
Co(3)–C(8)	1.766(16)	Co(3)–C(9)	1.816(17)
Co(1)–C(10)	1.902(14)	Co(2)–C(10)	1.883(11)
Co(3)–C(10)	1.901(11)	C(10)–C(11)	1.497(19)
C(11)–C(12)	1.49(2)	C(12)–C(13)	1.36(3)
C(13)–C(14)	1.45(4)	C(14)–C(15)	1.43(3)
C(11)–C(15)	1.55(3)	C(1)–O(1)	1.13(2)
C(2)–O(2)	1.13(2)	C(3)–O(3)	1.11(2)
C(4)–O(4)	1.14(2)	C(5)–O(5)	1.10(2)
C(6)–O(6)	1.12(2)	C(7)–O(7)	1.11(2)
C(8)–O(8)	1.13(2)	C(9)–O(9)	1.11(2)
Co(2)–Co(1)–Co(3)	60.2(1)	Co(1)–Co(2)–Co(3)	59.9(1)
Co(1)–Co(3)–Co(2)	59.9(1)	Co(2)–Co(1)–C(2)	96.6(5)
Co(2)–Co(1)–C(3)	99.5(4)	Co(3)–Co(1)–C(1)	98.3(5)
Co(3)–Co(1)–C(3)	98.9(5)	C(1)–Co(1)–C(2)	96.9(7)
C(1)–Co(1)–C(3)	101.2(7)	C(2)–Co(1)–C(3)	102.0(7)
Co(3)–Co(2)–C(5)	99.8(5)	Co(3)–Co(2)–C(6)	96.4(5)
Co(1)–Co(2)–C(4)	98.5(6)	Co(1)–Co(2)–C(5)	98.9(5)
C(4)–Co(2)–C(5)	102.5(6)	C(4)–Co(2)–C(6)	96.9(8)
C(5)–Co(2)–C(6)	101.2(7)	Co(1)–C(10)–Co(2)	80.7(5)
Co(1)–C(10)–Co(3)	80.2(5)	Co(2)–C(10)–Co(3)	81.1(4)
C(10)–C(11)–C(12)	114.9(12)	C(10)–C(11)–C(15)	112.8(11)
C(11)–C(12)–C(13)	109.8(18)	C(12)–C(13)–C(14)	111.5(20)
C(13)–C(14)–C(15)	107.1(23)	C(14)–C(15)–C(11)	106.5(17)
Co(1)–C(1)–O(1)	178.2(13)	Co(1)–C(2)–O(2)	175.8(15)
Co(1)–C(3)–O(3)	177.8(12)	Co(2)–C(4)–O(4)	178.5(15)
Co(2)–C(5)–O(5)	178.7(13)	Co(2)–C(6)–O(6)	176.9(14)
Co(3)–C(7)–O(7)	173.4(15)	Co(3)–C(8)–O(8)	177.8(13)
Co(3)–C(9)–O(9)	177.9(13)		

as axial. The three axial carbonyl groups, *trans* to the apical C(10) atom, show Co–C bonds [1.816-(17), 1.828(17) and 1.845(17) Å] longer than the ones corresponding to the equatorial carbonyls [in the range 1.749(16)–1.784(17) Å]. The structure of **II** is quite comparable to those of $Co_3(CO)_9(\mu_3\text{-}CH)$ [26] and $Co_3(CO)_9(\mu_3\text{-}C\text{–}CH_3)$ [27].

The cyclopentene ligand is regular with the double bond localized on the C(12)–C(13) bond [1.36(3) Å] and an 'envelope' conformation [the C(15) atom deviates 0.20(2) Å from the mean plane through the other four]. It is inclined with respect to the metal triangle, the dihedral angle between the planar moiety and the triangle being 129.8(6)°.

Supplementary Material

Coordinates of the hydrogen atoms, thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

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