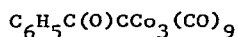


THE MOLECULAR STRUCTURE OF BENZOYLMETHYLIDYNETRICOBALT NONACARBONYL,



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Summary

The molecular structure of benzoylmethylidynetricobalt nonacarbonyl, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{CCo}_3(\text{CO})_9$, has been determined by single crystal X-ray crystallography. The sample crystallized from heptane forms as monoclinic prisms of space group $\text{P2}_1/\text{c}$, with $a = 8.836(2)$, $b = 14.097(10)$, $c = 16.514(3)$, $\beta = 103.37(6)$ and $Z = 2$. The final R value was 0.053. The structure is regular and normal but does not aid in explaining the interesting properties of this cluster.

Introduction

During the course of a study of the ground state electronic structure of alkylidynetricobalt nonacarbonyl complexes, $\text{RCCo}_3(\text{CO})_9$, using ^{59}Co NQR spectroscopy,¹ we encountered unexpectedly large differences in the electric field gradient at the three cobalt atoms when $\text{R} = \text{C}_6\text{H}_5\text{C}(\text{O})-$. This behavior was not observed in any of the other clusters we studied. In addition Seyferth, *et al.*,² have reported facile hydrogenation of the C=O bond in the organic portion of the molecule as well as thermal decarbonylation

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involving that group. In light of these interesting properties, an X-ray crystal structure determination of $C_6H_5C(O)CCO_3(CO)_9$ was undertaken and the results are reported here.

Experimental

Benzoylmethylidynetricobalt nonacarbonyl was prepared as described previously.³ The sample crystals on which the NQR spectrum was recorded were grown from hexane. Long black needles form which were not of high enough quality for single crystal X-ray diffraction. Well-formed high quality prisms were grown by slow evaporation (over a period of one week) of a heptane solution containing the complex. These prisms were used in the collection of the X-ray data. Crystals grown from hexane and heptane both melt at 65–67°C and have the same X-ray powder diffraction pattern within the limits of the camera used.

A prismatic crystal of violet-black $C_6H_5C(O)CCO_3(CO)_9$ with dimensions of about 0.20 x 0.17 x 0.15 mm was chosen for study. It was mounted with the longest dimension as the spindle axis.

The space group and related cell data are: Monoclinic, $P2_1/c$, $a = 8.836(2)$, $b = 14.097(10)$, $c = 16.514(3)$, $\beta = 103.37(6)$, $Z = 2$ and $\rho_{calc} = 1.78 \text{ gm/cm}^3$.

Intensity data were collected with Mo K_α radiation, using a 2θ scan rate of $1^\circ/\text{min}$ over a range of 1.75° , plus $K_{\alpha_1} - K_{\alpha_2}$, out of a maximum of 45° . A total of 2603 reflections were measured with 2452 being defined as observed. Reflections with $F_o < 1.5 \sigma_{F_o}$ were given zero weight in the refinement; reflection standard deviations were calculated based on counting statistics. No sample decomposition was detected during the data collection; no correction for absorption was deemed necessary.

The structure was resolved using direct method tangent refinement to locate the three cobalt atoms. Subsequent cycles of difference Fourier and least-squares refinements located all other non-hydrogen atoms. Anisotropic temperature factors were introduced and cycles of least-squares refinement continued. Hydrogen atoms were introduced with uniform isotropic temperature

factors, via calculation of their positions at the expected bond length.

$$R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|} \quad \text{and} \quad R_w = \left[\frac{\sum_w (|F_o| - |F_c|)^2}{\sum_w |F_o|^2} \right]^{1/2}$$

were minimized in the refinement cycles. The final R and R_w values are 0.053 and 0.054, respectively. No extinction correction was necessary. A final difference Fourier map showed no electron density greater than $0.5 \text{ e}^-/\text{\AA}^3$.

Results and Discussion

The structure determination produced the same molecular configuration that has been found for other $\text{RCCo}_3(\text{CO})_9$ complexes studied to date. Figures 1 and 2 are ORTEP drawings of the molecule in two different orientations. Tables 1 and 2 contain the bond distances and angles, Table 3 contains x, y, z atomic coordinates and Table 4 contains the atomic thermal parameters. The structure

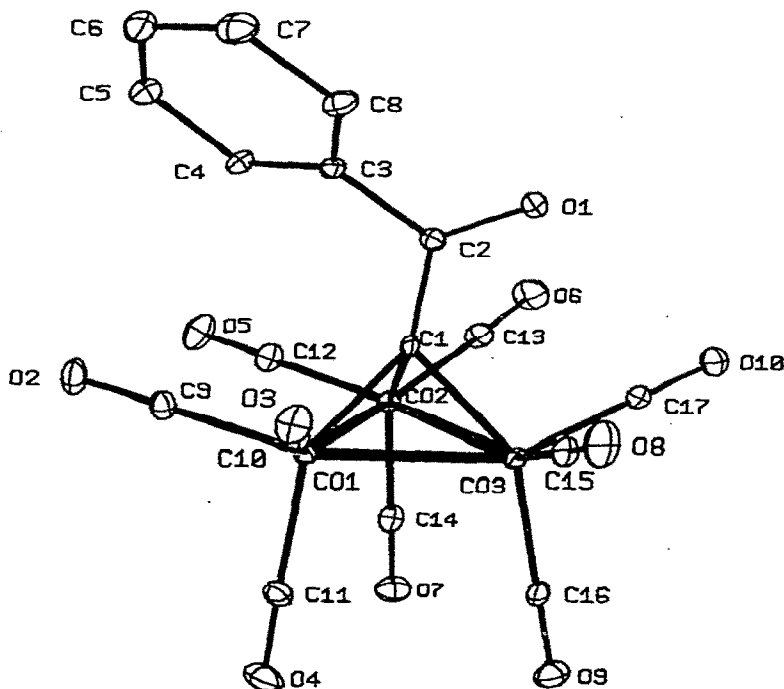


Figure 1. ORTEP plot of benzoylmethylidyne tricobalt nonacarbonyl showing 50% probability ellipsoids.

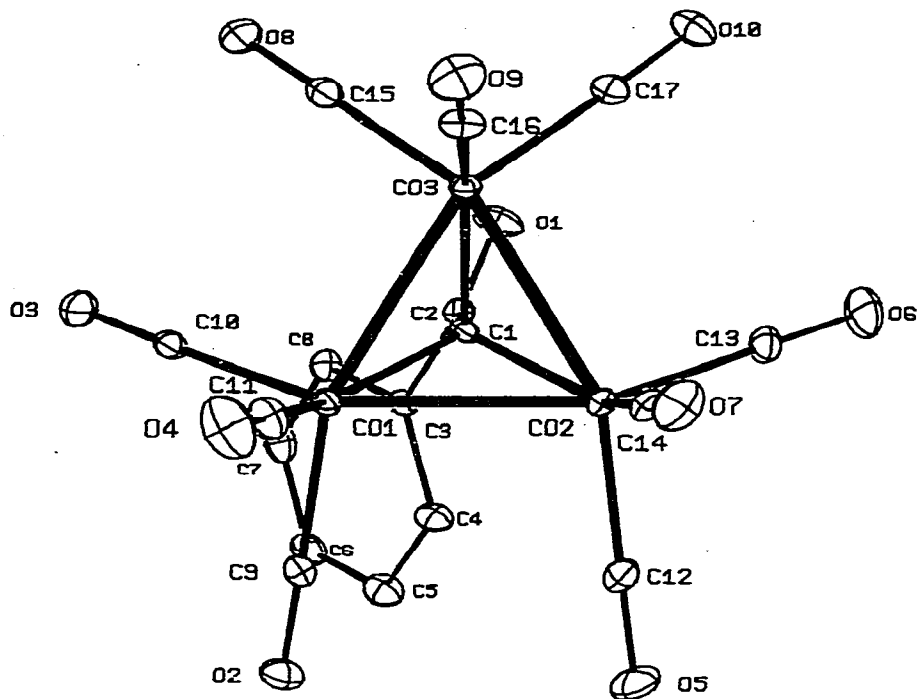


Figure 2. ORTEP plot viewed perpendicular to the Co_3 plane.

reveals the Co_3 trigonal plane to be regular and normal with Co-Co bond lengths of 2.472(5) Å. These distances fall in the range of 2.465–2.498 Å found in other $\text{RCo}_3(\text{CO})_9$ clusters.⁴⁻¹¹ The methylidyne carbon atom, C(1), lies at a distance of 1.89–1.92 Å from the cobalt atoms. The range of Co-C(1) distances reported before is about 1.80–2.0 Å.⁴⁻¹¹ The benzene ring is regular and normal. The ketone carbon atom, C(2), lies slightly off a line passing perpendicular to the Co_3 plane and through the C(1) carbon as can be seen in Figure 2. If C(2) had a very substantial deviation from this line it might indicate that the cobalt atoms and electrons in the C(1)–C(2) bond directly interact with one another as a π -ethylidyne-cobalt interaction. This does not appear to be the case. Furthermore, the ketone oxygen atom, O(1), does not interact with the cobalt atom nearest to it, Co(3), because the distance between them is 3.29 Å. This distance exceeds the sum of the estimated van der Waals radii for O and Co. Thus, the crystal structure does not explain the unusual NQR spectrum in which the cobalt atoms have considerable

Table 1: Bond Distances (\AA) and Their Standard Deviations in Parentheses

| | | | |
|-------------|-----------|-------------|----------|
| Co(1)-Co(2) | 2.476(1) | Co(1)-C(9) | 1.811(8) |
| Co(1)-Co(3) | 2.467(2) | Co(1)-C(10) | 1.781(8) |
| Co(2)-Co(3) | 2.467(1) | Co(1)-C(11) | 1.836(8) |
| Co(1)-C(1) | 1.891(6) | Co(2)-C(12) | 1.813(9) |
| Co(2)-C(1) | 1.893(6) | Co(2)-C(13) | 1.798(8) |
| Co(3)-C(1) | 1.921(6) | Co(2)-C(14) | 1.811(7) |
| C(1)-C(2) | 1.473(8) | Co(3)-C(15) | 1.780(9) |
| C(2)-O(1) | 1.235(9) | Co(3)-C(16) | 1.845(6) |
| C(2)-C(3) | 1.495(8) | Co(3)-C(17) | 1.800(8) |
| C(3)-C(4) | 1.380(10) | | |
| C(3)-C(8) | 1.379(10) | | |
| C(4)-C(5) | 1.420(10) | | |
| C(5)-C(6) | 1.370(15) | | |
| C(6)-C(7) | 1.393(14) | | |
| C(7)-C(8) | 1.436(11) | | |
| C(9)-O(2) | 1.122(10) | | |
| C(10)-O(3) | 1.136(10) | | |
| C(11)-O(4) | 1.126(10) | | |
| C(12)-O(5) | 1.122(11) | | |
| C(13)-O(6) | 1.132(11) | | |
| C(14)-O(7) | 1.145(9) | | |
| C(15)-O(8) | 1.141(11) | | |
| C(16)-O(9) | 1.107(8) | | |
| C(17)-O(10) | 1.135(9) | | |

electric field gradient inequivalence. The very highly regular molecular structure in the crystal on which the X-ray data were collected could not produce the inequivalence of the cobalt atoms that is necessary to comprehend the NQR data. The NQR spectrum was recorded on a sample grown from hexane while the crystals used in the X-ray work were grown from heptane. The difference in the results of the NQR and X-ray work might arise from the fact that the two samples are not indeed the same. This is in spite of the fact that both melted at the same temperature. Additional work will be needed to resolve this question.

Unusually facile hydrogenation of the keto C=O bond occurs in this

(continued on p. 404)

Table 2: Bond Angles ($^{\circ}$) with Their Standard Deviations in Parentheses

| | | | |
|-------------------|------------|-------------------|------------|
| Co(2)-Co(1)-Co(3) | 59.85(4) | C(15)-Co(3)-Co(1) | 96.24(23) |
| Co(1)-Co(2)-Co(3) | 59.89(4) | C(15)-Co(3)-Co(2) | 148.40(23) |
| Co(1)-Co(3)-Co(2) | 60.25(4) | C(16)-Co(3)-C(1) | 146.36(29) |
| C(1)-Co(1)-Co(3) | 50.19(17) | C(16)-Co(3)-Co(1) | 102.95(23) |
| C(1)-Co(1)-Co(2) | 49.16(20) | C(16)-Co(3)-Co(2) | 103.94(24) |
| C(1)-Co(2)-Co(1) | 49.10(18) | C(17)-Co(3)-C(1) | 101.41(28) |
| C(1)-Co(2)-Co(3) | 50.20(18) | C(17)-Co(3)-Co(1) | 149.84(23) |
| C(1)-Co(3)-Co(1) | 49.15(17) | C(17)-Co(3)-Co(2) | 97.05(26) |
| C(1)-Co(3)-Co(2) | 49.21(20) | O(2)-C(9)-Co(1) | 178.85(71) |
| C(9)-Co(1)-C(1) | 107.9(31) | O(3)-C(10)-Co(1) | 177.69(59) |
| C(9)-Co(1)-Co(2) | 98.41(26) | O(4)-C(11)-Co(1) | 178.43(70) |
| C(9)-Co(1)-Co(3) | 155.52(26) | O(5)-C(12)-Co(2) | 178.58(65) |
| C(10)-Co(1)-C(1) | 99.41(29) | O(6)-C(13)-Co(2) | 178.15(78) |
| C(10)-Co(1)-Co(2) | 148.36(21) | O(7)-C(14)-Co(2) | 177.83(75) |
| C(10)-Co(1)-Co(3) | 99.20(21) | O(8)-C(15)-Co(3) | 177.85(67) |
| C(11)-Co(1)-C(1) | 142.48(29) | O(9)-C(16)-Co(3) | 178.82(69) |
| C(11)-Co(1)-Co(2) | 101.76(26) | O(10)-C(17)-Co(3) | 178.24(73) |
| C(11)-Co(1)-Co(3) | 97.12(25) | Co(1)-C(1)-Co(3) | 80.66(22) |
| C(12)-Co(2)-C(1) | 109.45(29) | Co(1)-C(1)-Co(2) | 81.74(23) |
| C(12)-Co(2)-Co(1) | 96.86(26) | Co(2)-C(1)-Co(3) | 80.59(21) |
| C(12)-Co(2)-Co(3) | 155.38(25) | Co(1)-C(1)-C(2) | 132.64(45) |
| C(13)-Co(2)-C(1) | 101.85(30) | Co(2)-C(1)-C(2) | 136.61(50) |
| C(13)-Co(2)-Co(1) | 150.58(25) | Co(3)-C(1)-C(2) | 124.13(47) |
| C(13)-Co(2)-Co(3) | 99.74(27) | C(1)-C(2)-O(1) | 121.04(55) |
| C(14)-Co(2)-C(1) | 137.81(32) | C(3)-C(2)-O(1) | 118.75(54) |
| C(14)-Co(2)-Co(1) | 98.81(25) | C(4)-C(3)-C(2) | 121.07(60) |
| C(14)-Co(2)-Co(3) | 92.29(27) | C(8)-C(3)-C(2) | 116.95(62) |
| C(15)-Co(3)-C(1) | 99.82(30) | C(8)-C(3)-C(4) | 121.98(59) |
| | | C(3)-C(4)-C(5) | 119.54(74) |
| | | C(4)-C(5)-C(6) | 119.83(87) |
| | | C(5)-C(6)-C(7) | 120.48(77) |
| | | C(6)-C(7)-C(8) | 120.23(77) |
| | | C(7)-C(8)-C(9) | 117.93(74) |

Table 3: Fractional Atomic Coordinates ($\times 10^4$) with Standard Deviations
in Parentheses

| <u>Atom Type</u> | <u>x</u> | <u>y</u> | <u>z</u> |
|------------------|----------|----------|----------|
| Co(1) | 3405(1) | 3127(1) | 7069(1) |
| Co(2) | 1336(1) | 4240(1) | 7245(1) |
| Co(3) | 2996(1) | 4626(1) | 6277(1) |
| C(1) | 3520(7) | 4395(4) | 7455(3) |
| C(2) | 4720(7) | 4922(5) | 8053(4) |
| C(3) | 5547(8) | 4466(4) | 8850(4) |
| C(4) | 4739(9) | 3974(5) | 8337(4) |
| C(5) | 5559(12) | 3567(6) | 10099(5) |
| C(6) | 7146(12) | 2647(6) | 10334(5) |
| C(7) | 7959(10) | 4141(7) | 9839(6) |
| C(8) | 7141(9) | 4568(6) | 9074(5) |
| C(9) | 3393(9) | 2357(5) | 7945(5) |
| C(10) | 5402(9) | 2935(5) | 7082(4) |
| C(11) | 2349(9) | 2353(5) | 6234(5) |
| C(12) | 836(9) | 3640(6) | 8118(5) |
| C(13) | 707(9) | 5414(6) | 7442(5) |
| C(14) | - 222(8) | 3816(5) | 6409(5) |
| C(15) | 4896(9) | 4691(5) | 6087(4) |
| C(16) | 1830(8) | 4247(5) | 5252(4) |
| C(17) | 2671(8) | 5888(5) | 6244(4) |
| O(1) | 5093(7) | 5735(4) | 7898(3) |
| O(2) | 3413(8) | 1879(4) | 8491(4) |
| O(3) | 6689(7) | 2835(4) | 7111(4) |
| O(4) | 1693(8) | 1896(4) | 5710(4) |
| O(5) | 497(7) | 3267(5) | 8650(4) |
| O(6) | 299(8) | 6143(5) | 7584(4) |
| O(7) | -1172(6) | 3539(4) | 5867(4) |
| O(8) | 6126(7) | 4751(4) | 5986(4) |
| O(9) | 1154(6) | 4019(4) | 4633(3) |
| O(10) | 2502(7) | 6686(4) | 6219(4) |

Table 4: Anisotropic Thermal Parameters^a ($\times 10^4$) with Estimated Standard Deviations in Parentheses

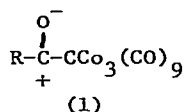
| Atom Type | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|-----------|----------|----------|----------|----------|----------|----------|
| Co(1) | 481(6) | 331(6) | 442(6) | 278(39) | 116(4) | -106(38) |
| Co(2) | 465(6) | 465(7) | 441(6) | 425(40) | 162(4) | 054(40) |
| Co(3) | 481(6) | 413(6) | 342(6) | 130(40) | 112(4) | 371(37) |
| C(1) | 587(40) | 276(33) | 345(32) | 73(29) | 103(29) | 82(26) |
| C(2) | 556(40) | 430(40) | 442(39) | -59(31) | 129(32) | -39(31) |
| C(3) | 627(42) | 390(34) | 356(33) | 45(31) | 48(30) | -35(27) |
| C(4) | 895(55) | 650(46) | 362(37) | -16(41) | 55(36) | 56(33) |
| C(5) | 1158(76) | 761(59) | 566(49) | -14(54) | 93(49) | 20(43) |
| C(6) | 1146(77) | 707(56) | 671(53) | 138(54) | 52(52) | 43(43) |
| C(7) | 739(53) | 980(63) | 898(63) | 230(48) | -132(48) | -136(53) |
| C(8) | 614(49) | 766(54) | 565(45) | 112(42) | 6(38) | -47(40) |
| C(9) | 742(49) | 464(42) | 761(52) | 119(37) | 298(40) | 70(40) |
| C(10) | 677(49) | 410(38) | 477(38) | 69(35) | 136(34) | 88(29) |
| C(11) | 737(55) | 514(45) | 706(51) | 54(41) | 90(42) | -75(41) |
| C(12) | 599(46) | 783(50) | 705(52) | 78(40) | 297(41) | 93(43) |
| C(13) | 637(47) | 643(51) | 630(47) | 148(40) | 194(38) | -50(39) |
| C(14) | 434(41) | 705(46) | 731(50) | 60(36) | 270(38) | 152(39) |
| C(15) | 670(50) | 521(45) | 592(45) | 51(39) | 125(38) | 106(35) |

| | | | | | | |
|-------|----------|----------|----------|----------|----------|----------|
| C(16) | 641(44) | 542(45) | 469(37) | -124(36) | 109(32) | 103(33) |
| C(17) | 655(46) | 547(47) | 492(41) | 3(37) | 79(33) | 67(35) |
| O(1) | 1259(45) | 522(33) | 670(33) | -313(31) | -126(31) | 89(27) |
| O(2) | 1434(55) | 702(39) | 910(41) | 184(37) | 558(38) | 363(35) |
| O(3) | 612(37) | 908(41) | 940(42) | 178(32) | 288(32) | 205(33) |
| O(4) | 1114(50) | 699(40) | 1046(48) | -23(35) | -182(39) | -363(37) |
| O(5) | 1056(48) | 1435(56) | 868(42) | 49(42) | 558(38) | 431(41) |
| O(6) | 1209(56) | 803(43) | 1160(52) | 365(40) | 318(43) | -245(38) |
| O(7) | 573(32) | 1079(46) | 818(38) | -133(31) | 79(29) | -192(34) |
| O(8) | 1260(45) | 522(33) | 670(33) | -314(31) | -216(31) | 89(27) |
| O(9) | 841(38) | 1033(44) | 567(29) | -142(33) | 58(26) | -108(29) |
| O(10) | 1187(49) | 504(34) | 852(40) | 90(32) | 98(34) | 116(29) |

^aAnisotropic thermal parameters are root-mean square amplitude displacements expressed in Å, ($\times 10^4$). The form of the anisotropic temperature factor expression is

$$\exp[2\pi^2(U_{11}^2 h^2 a^2 + U_{22}^2 k^2 b^2 + U_{33}^2 l^2 c^2 + 2U_{12} hka b \cos \gamma + 2U_{13} hla c \cos \beta + 2U_{23} klb c \cos \alpha)].$$

type of compound without a catalyst.² Thermal decarbonylation is also observed to take place.² A resonance form of the type shown in structure (1) has been



suggested might exist in these systems,^{2,12} and that steric considerations may weaken the C(1)-C(2) bond. It was hoped that the molecular structure would provide evidence of these effects at least in so far as they can affect the bond lengths. The C=O bond distance in the keto unit of this cluster is 1.235(9) Å which compares closely to the distance of 1.215 Å in organic ketones of the type C₆H₅C(O)R.¹³ Similarly, the C=O bond length in [(CO)₉Co₃C]₂CO is found to be 1.24 Å.⁶ A C(1)-C(2) bond length of 1.473(8) Å observed here in C₆H₅C(O)CCo₃(CO)₉ is close in value to the bond length of 1.48(2) Å between the apical carbon atom and the ipso carbon atom of benzene in C₆H₅CCo₃(CO)₆-π-mesitylene.¹⁴ The C-C bond lengths in [(CO)₉Co₃C]₂CO are 1.60 and 1.42 Å but the difference is not believed to be real.⁶ Carbon(1) is believed to be more of an sp hybridized carbon atom than an sp³ carbon atom.^{1,15,16} In this case the C(1)-C(2) bond length should be similar to the lengths in other carbon-carbon bonds involving sp-sp² linkages. Two carbon atoms hybridized as sp and sp² bond with a distance of 1.45±0.02 Å,¹³ which is very similar to the C(1)-C(2) bond of 1.47 Å in the cluster examined here. Hence neither the C=O nor C-C bond lengths show clear evidence of structure (1) in the ground state.

The X-ray data reveal nothing unusual about this sample of C₆H₅C(O)CCo₃(CO)₉ compared to other clusters, at least as far as the ground state electronic structure is concerned. Since reaction mechanisms can depend strongly on kinetic excited states, the X-ray data provide no information about the course of reactions apart from suggesting that the ground state electronic factors do not contribute dramatically to the mechanism. It is clear that a great deal more information will be needed to fully understand the perplexing properties of these clusters.

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