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Transition Metal Methylene Complexes, VII[1)]
Studies on Metal – Metal Bonds, V[2)]

Preparation and Molecular Structure of a Carbonylcobalt Complex Containing a Novel Carbocyclic μ-Methylene Ligand

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Dicarbonyl(η^5-cyclopentadienyl)cobalt (**1**) reacts with 2-diazo-1,3-dioxoindane (**2**) under thermal conditions (boiling benzene) to yield the dinuclear cobalt complex **3** which contains the carbene derived from **2** as a bridging ligand. An x-ray diffraction study proved that both the cyclopentadienyl rings are oriented *trans* to each other, which is also true for the two metal – carbonyl groups. While four-bonded, the methylene carbon is highly distorted from tetrahedral geometry [∢Co(1) – C(3) – Co(2): 79.0(1)°, ∢C(4) – C(3) – C(11): 104.3(3)°]. The cobalt – cobalt distance is 247.5(1) pm and the Co – C(C_5H_5) and Co – C(CO) distances and angles are normal. The μ-1,3-dioxoindane-2-ylidene backbone is bent by 2° along the vector joining the two carbonyl carbon atoms of the dione system.

Übergangsmetall – Methylen-Komplexe, VII[1)]
Studien über Metall – Metall-Bindungen, V[2)]
Darstellung und Molekülstruktur eines Carbonylcobalt-Komplexes mit einem neuartigen carbocyclischen μ-Methylen-Liganden

Dicarbonyl(η^5-cyclopentadienyl)cobalt (**1**) reagiert mit 2-Diazo-1,3-dioxoindan (**2**) unter thermischen Bedingungen (siedendes Benzol) unter Bildung des zweikernigen Cobalt-Komplexes **3**, der das von **2** abgeleitete Carben als Brückenliganden enthält. Eine Röntgenstrukturanalyse wies nach, daß die beiden Cyclopentadienyl-Ringe ebenso wie die beiden Carbonyl-Gruppen *trans*-Positionen zueinander einnehmen. Trotz seiner vier Bindungspartner weist das Methylen-Kohlenstoffatom eine sehr stark verzerrte tetraedrische Konfiguration auf [∢Co(1) – C(3) – Co(2): 79.0(1)°, ∢C(4) – C(3) – C(11): 104.3(3)°]. Der Cobalt – Cobalt-Abstand beträgt 247.5(1) pm; die Abstände und Winkel der Co – C(C_5H_5)- sowie Co – C(CO)-Bausteine sind normal. Das μ-1,3-Dioxoindan-2-yliden-Gerüst ist entlang der Verbindungslinie zwischen den beiden Carbonyl-Kohlenstoffatomen des Dion-Systems um 2° abgewinkelt.

Transition metal carbonyls containing bridging carbenes have only recently been recognized as easily accessible, thermally stable compounds[1–13)]. Probably the most reliable way into this hitherto little investigated class of compounds is through thermal as well as photochemical reactions of certain metal carbonyl derivatives with diazoalka-

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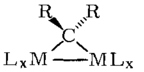
nes. By this general route, novel μ-methylene complexes have been synthesized which do not have analogues in organometallic chemistry[1,2,4,7-12]. Among them are the first transition metal compounds containing methylene, CH_2, as bridging ligand[7-9,13]. These compounds **A** are not only interesting as a novel class of organometallics but also as

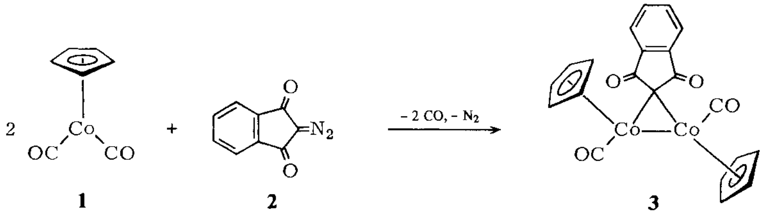


A

test cases of the theory of bonding of bridged carbenes[14] as well as for spectroscopic studies[12,13]. The reason for this wide range of interest in these substances is that our bridged methylene complexes are formally derived from simple transition metal carbonyls containing μ-carbonyl groups instead of μ-methylene functions. Thermal stabilities and other physical properties (e. g. solubilities, volatilities) are very similar for both classes of compounds, but they behave quite differently in chemical reactions. In order to get some more insight into the bondings of bridged methylene transition metal compounds, we synthesized a binuclear cyclopentadienyl carbonyl complex of cobalt containing 1,3-dioxoindane-2-ylidene as the bridging ligand. This carbene, derived from 2-diazo-1,3-dioxoindane (**2**)[15], has not been stabilized by co-ordination to metals before.

A. Synthetic and Spectroscopic Results

Compound **3** has been prepared by reaction of dicarbonyl(η^5-cyclopentadienyl)cobalt (**1**) with 2-diazo-1,3-dioxoindane (**2**) in boiling benzene. Although the organic carbene precursor is thermally stable up to about 150°C, it reacts with **1** smoothly under the reaction conditions employed here (formula 1):



1 **2** **3** (1)

Table 1. Selected Spectroscopic Data of the Dinuclear μ-[1,3-Dioxoindane-2-ylidene] Cobalt Complex **3**

IR:	ν(M–)C≡O: 1999 vst, 1986 vst; νC=O: 1680 w-m, 1651 st, 1588 cm^{-1} m [KBr] ν(M–)C≡O: 1990 vst; νC=O: 1714 st-vst, 1693 vst [CH_2Cl_2]
^1H NMR:	τC_5H_5: 5.03 (singlet, rel. int. 5); τC_6H_4: 2.37 (pseudosinglet, rel. int. 2) [solvent: $CDCl_3$; internal TMS; +33°C]
MS[a]:	$M^{+\cdot}$ (*m/e* 448; rel. int. 15%), $[M - CO]^{+\cdot}$ (420; 100), $[M - 2\,CO]^{+\cdot}$ (392; 42), $[M - 3\,CO]^{+\cdot}$ (364; 86), $[M - 4\,CO]^{+\cdot}$ (336; 66), $[(C_5H_5)_2Co(C_9H_4O_2)]^{+\cdot}$ (333; 64), $[M - 4\,CO - Co]^{+\cdot} \equiv [(C_5H_5)_2Co(C_7H_4)]^{+\cdot}$ (277; 57) [$P = 70$ eV; $T_Q = 130°C$, $T_E = 150°C$].

[a] Fragmentation pattern proved by the occurence of the corresponding „metastable“ peaks.

The new compound is a brown crystalline, air-stable substance which decomposes in a sealed capillary above ca. 145°C. **3** is soluble in benzene or more polar solvents (diethylether, methylenechloride); the dark-brown solutions are slightly air-sensitive and should be kept under an inert gas atmosphere.

μ-[1,3-Dioxoindane-2-ylidene]-bis[carbonyl(η^5-cyclopentadienyl)cobalt](*Co–Co*) (**3**) has been characterized by elemental analyses and osmometric molecular weight determination (see Experimental Part) and by its IR, ^{1}H NMR and mass spectra (table 1). While these data establish the composition of **3** unequivocally, we decided to undertake an accurate crystal structure analysis in order to determine whether the cyclopentadienyl rings are oriented *cis* or *trans* to each other and also to examine the nature of the bridging ligand.

B. Crystal Structure Determination

Compound **3** crystallizes monoclinic from diethylether. The crystal selected for data collection was mounted on an Enraf-Nonius automated diffractometer and intensity data was collected and reduced as described previously[16,17].

The position of one cobalt atom was found by the Patterson method, and all of the remaining non-hydrogen atoms were found in subsequent difference Fourier maps. A refinement of the non-hydrogen atoms with individual isotropic temperature factors yielded an agreement factor of

$$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.0600$$

The assignment of anisotropic temperature factors and further blocked least squares refinement reduced the agreement factor to $R = 0.041$. At this stage theoretical hydrogen positions were calculated (C–H 108 pm) and refined with individual isotropic temperature factors ($R = 0.0374$).

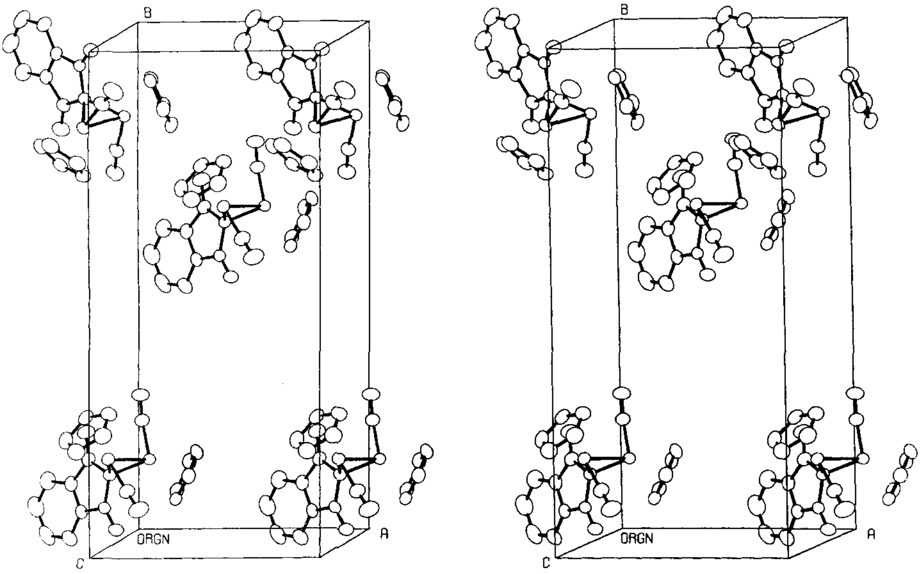


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Figure 1. Packing Diagram of the 1,3-Dioxoindane-2-ylidene Complex **3**

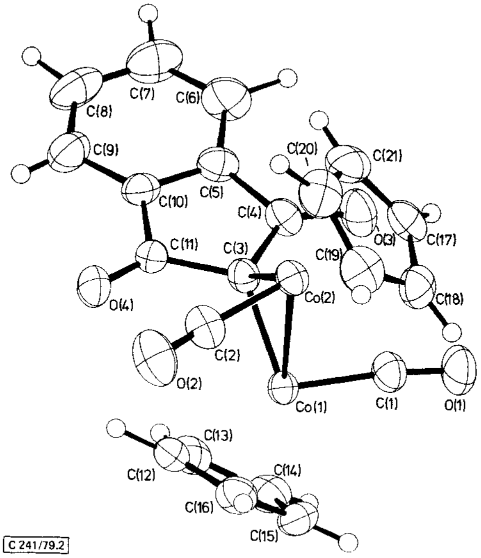

Figure 2. ORTEP Representation of **3**. The Thermal Ellipsoids of the Atoms Except Hydrogen Correspond to 50% Probability

Table. 2. Atomic Coordinates and Thermal Parameters of **3** ($C \times 10^3$, $O \times 10^3$, $Co \times 10^4$, $H \times 10^2$)

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
CO1	-.07852(0)	-.14645(2)	-.14790(0)	308(2)	256(1)	254(2)	13(2)	86(1)	17(2)
CO2	.05591(5)	-.15803(2)	-.35302(7)	347(2)	301(2)	277(2)	33(2)	116(2)	-20(2)
C1	-.0255(4)	-.2177(2)	-.0669(5)	44(2)	35(2)	38(2)	4(1)	14(1)	8(1)
C2	-.0493(4)	-.1034(2)	-.4879(5)	52(2)	45(2)	29(1)	7(2)	15(1)	-1(1)
O1	-.0366(3)	-.2652(1)	-.0150(5)	68(2)	38(1)	66(2)	8(1)	25(2)	20(1)
O2	-.1205(4)	-.0731(2)	-.5897(4)	82(2)	60(2)	35(1)	21(2)	15(1)	14(1)
O3	.2497(3)	-.1854(1)	.0876(4)	53(2)	39(1)	44(1)	8(1)	0(1)	6(1)
O4	.0523(3)	-.0126(1)	-.2372(4)	46(1)	33(1)	56(2)	2(1)	11(1)	11(1)
C3	.1037(3)	-.1147(1)	-.1257(4)	29(1)	28(1)	30(1)	2(1)	5(1)	0(1)
C4	.2251(3)	-.1355(2)	.0236(4)	34(1)	38(1)	30(1)	5(1)	5(1)	-2(1)
C5	.3155(3)	-.0840(2)	.0963(4)	31(2)	47(2)	34(2)	-1(1)	7(1)	-7(1)
C6	.4432(5)	-.0824(2)	.2292(6)	43(2)	64(3)	50(2)	-2(2)	-2(2)	-8(2)
C7	.5051(5)	-.0278(3)	.2757(7)	46(2)	84(3)	59(3)	-21(2)	1(2)	-16(2)
C8	.4408(5)	.0238(3)	.1941(7)	55(3)	68(3)	69(3)	-31(2)	22(2)	-21(2)
C9	.3154(5)	.0219(2)	.0589(6)	48(2)	46(2)	60(2)	-15(2)	20(2)	-8(2)
C10	.2538(3)	-.0329(2)	.0104(5)	32(1)	39(2)	42(2)	-5(1)	16(1)	-5(1)
C11	.1237(3)	-.0487(1)	-.1327(4)	30(1)	31(1)	37(1)	-1(1)	12(1)	-1(1)
C12	-.2045(4)	-.0728(2)	-.2317(5)	33(2)	37(2)	48(2)	6(1)	15(1)	5(1)
C13	-.1691(4)	-.0790(2)	-.0445(5)	43(2)	42(2)	48(2)	5(1)	18(2)	-12(1)
C14	-.2168(4)	-.1343(2)	-.0108(5)	43(2)	55(2)	44(2)	6(2)	23(2)	5(2)
C15	-.2842(4)	-.1617(2)	-.1771(6)	34(2)	45(2)	55(2)	-6(1)	14(2)	7(2)
C16	-.2778(4)	-.1237(2)	-.3119(5)	32(2)	49(2)	40(2)	2(1)	2(1)	4(2)
C17	.1715(5)	-.2354(2)	-.2805(6)	48(2)	38(2)	51(2)	14(2)	17(2)	-4(2)
C18	.0458(4)	-.2498(2)	-.4122(6)	53(2)	33(2)	52(2)	0(2)	22(2)	-8(1)
C19	.0385(6)	-.2163(2)	-.5636(6)	64(3)	49(2)	39(2)	1(2)	18(2)	-15(2)
C20	.1612(5)	-.1829(2)	-.5273(6)	74(3)	49(2)	55(2)	2(2)	42(2)	-8(2)
C21	.2425(5)	-.1945(2)	-.3513(7)	43(2)	53(2)	68(3)	4(2)	27(2)	-15(2)
H6	.490(8)	-.123(3)	.296(9)	95(21)					
H7	.591(7)	-.020(3)	.340(9)	92(21)					
H8	.504(6)	.055(3)	.237(8)	69(15)					
H9	.266(5)	.054(2)	.000(6)	51(13)					
H12	-.180(4)	-.037(2)	-.291(6)	41(11)					
H13	-.119(5)	-.053(2)	.044(7)	55(13)					
H14	-.196(9)	-.165(3)	.105(10)	96(24)					
H15	-.317(6)	-.201(3)	-.190(7)	71(16)					
H16	-.314(5)	-.133(2)	-.434(7)	48(12)					
H17	.201(6)	-.247(3)	-.176(8)	64(16)					
H18	-.021(4)	-.273(2)	-.401(6)	34(10)					
H19	-.017(6)	-.218(2)	-.638(8)	56(17)					
H20	.188(4)	-.156(1)	-.615(5)	15(3)					
H21	.327(6)	-.177(3)	-.306(7)	66(16)					

$T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2\ klb^*c^*U_{23}]$

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In the final stages of refinement a full matrix least squares routine was used. The small correction factor in the weighting scheme was calculated so as to give a minimum variance in $w \cdot (F_o - F_c)^2$ as a function of F_o[18]. Refinement of all positional and thermal parameters yielded the final agreement factors given in the Experimental Part.

All of the parameter shifts in the last cycle of least squares were less than 0.1 times their respective estimated standard deviations. In a final difference Fourier map, the largest residual peak was 0.63e/Å^3. All of the routines used in structure refinement were taken from the SHELX-76 system of computer programs[18)].

Inasmuch as the correct space group is *Cc*, the crystals are polar but the contents of the unit cell consists of a racemic mixture of two of the four possible diastereoisomers. The current pair (fig. 1) consists of pairs of (*R,R*) and (*S,S*) configurated cobalt centers. Also, as can be seen from the packing diagram (fig. 1), the enantiomers of this mixture are arranged in a head-to-tail fashion. Therefore, to correctly identify the chirality of the crystal used in this study, the refinement procedure described above was carried out, once more, using the inverse coordinates of the atoms. This procedure resulted in agreement factors of $R(F) = 0.0355$ and $R_w(F) = 0.0346$, which is, decidedly, an inferior result to the previous one. Thus, the crystallographic parameters listed in tables 2 and 3 are those of the structural refinement with the smaller values of $R(F)$ and $R_w(F)$.

As shown in table 3 and figure 2, the geometries about the two cobalt atoms are almost identical. Also, the deviations of the atoms from the Co(1) – C(3) – Co(2) plane are nearly symmetrical. Perfect C_2 symmetry is lost, however, due to a bending of the dioxoindanylidene moiety, into two planes, about the C(4)···C(11) vector. It is, in fact, this bending which prevents the molecules from lying at the two-fold axis of the space group *C2/c* which, otherwise, they would have crystallized into (*vide supra*). At first, one might suspect that this distortion is the result of steric hindrance between the oxygens of the carbonyl groups and the oxygens of the dioxoindanylidene ligand. However, the average contact distance between such atoms is approximately 30 pm *longer* than the normal oxygen-oxygen van der Waals contacts[19)] of 280 pm. Actually, the

Table 3. Molecular Geometry of **3**

(a) Intra-Molecular distances (pm)

Co(1) - Co(2)	247.5(1)		
Co(1) - C(1)	174.5(4)	Co(2) - C(2)	177.9(4)
Co(1) - C(3)	191.6(4)	Co(2) - C(3)	197.3(4)
Co(1) - C(12)	210.4(4)	Co(2) - C(17)	206.8(5)
Co(1) - C(13)	211.8(5)	Co(2) - C(18)	212.0(5)
Co(1) - C(14)	211.4(6)	Co(2) - C(19)	207.3(6)
Co(1) - C(15)	213.0(5)	Co(2) - C(20)	206.2(7)
Co(1) - C(16)	214.2(4)	Co(2) - C(21)	204.5(6)
O(1) - C(1)	114.2(5)	O(3) - C(4)	112.9(5)
O(2) - C(2)	113.4(6)	O(4) - C(11)	112.4(5)
C(3) - C(4)	149.3(5)	C(7) - C(8)	139.8(9)
C(4) - C(5)	148.7(6)	C(8) - C(9)	138.5(7)
C(5) - C(6)	139.1(6)	C(9) - C(10)	138.7(6)
C(5) - C(10)	137.8(6)	C(10) - C(11)	149.3(5)
C(6) - C(7)	138.3(9)	C(11) - C(3)	150.6(5)
C(6) - H(6)	114(8)	C(8) - H(8)	95(7)
C(7) - H(7)	99(6)	C(9) - H(9)	88(8)
C(12) - H(12)	105(5)	C(17) - H(17)	110(9)
C(13) - H(13)	92(6)	C(18) - H(18)	93(6)
C(14) - H(14)	121(12)	C(19) - H(19)	55(6)
C(15) - H(15)	88(8)	C(20) - H(20)	100(4)
C(16) - H(16)	92(6)	C(21) - H(21)	91(7)
C (6) - H (6)	114(8)	C(7) - H(7)	98(6)
C (8) - H (8)	95(7)	C(9) - H(9)	89(8)
C(12) - H(12)	105(5)	C(17) - H(17)	117(11)
C(13) - H(13)	92(6)	C(18) - H(18)	93(6)
C(14) - H(14)	124(11)	C(19) - H(19)	55(6)
C(15) - H(15)	88(8)	C(20) - H(20)	100(4)
C(16) - H(16)	91(7)	C(21) - H(21)	91(7)

(b) Selected nonbonding contact distances (pm)

O(1) - H(17)	272(13)	O(2) - H(12)	275.(6)
O(1) - O(3)	308.8(5)	O(2) - O(4)	310.1(5)
O(3) - C(1)	279.7(6)	O(4) - O(2)	281.3(5)
O(3) - H(17)	215(11)	O(4) - H(12)	234(5)

(c) Intra-molecular angles(°)

C(1) - Co(1) - Co(2)	89.4(2)	C(2) - Co(2) - Co(1)	86.6(2)
C(3) - Co(1) - Co(2)	51.5(1)	C(3) - Co(2) - Co(1)	49.5(1)
C(3) - Co(1) - C(1)	99.4(2)	C(3) - Co(2) - C(2)	96.5(2)
O(1) - C(1) - Co(1)	173.1(5)	O(2) - C(2) - Co(2)	172.3(4)
Co(1) -C(3) - Co(2)	79.0(1)	C(4) - C(3) - C(11)	104.3(3)
O(3) - C(4) - C(3)	128.7(4)	C(7) - C(8) - C(9)	121.0(6)
O(3) - C(4) - C(5)	122.5(3)	C(8) - C(9) - C(10)	118.0(5)
C(3) - C(4) - C(5)	108.8(3)	C(5) - C(10)- C(9)	120.9(4)
C(4) - C(5) - C(6)	129.2(4)	C(5) - C(10) - C(11)	109.4(3)
C(4) - C(5) - C(10)	109.3(3)	C(9) - C(10) - C(11)	129.7(4)
C(6) - C(5) - C(10)	121.4(4)	O(4) - C(11) - C(10)	123.4(3)
C(5) - C(6) - C(7)	117.9(5)	O(4) - C(11) - C(3)	128.4(3)
C(6) - C(7) - C(8)	120.6(5)	C(10)- C(11)- C(3)	108.1(3)
C(12) - C(13) - C(14)	107.6(4)	C(17) - C(18) - C(19)	106.3(5)
C(13) - C(14) - C(15)	108.1(5)	C(18) - C(19) - C(20)	109.2(5)
C(14) - C(15) - C(16)	108.0(4)	C(19) - C(20) - C(21)	107.7(6)
C(15) - C(16) - C(12)	108.0(4)	C(20) - C(21) - C(17)	107.6(5)
C(16) - C(12) - C(13)	108.3(4)	C(21) - C(17) - C(18)	109.2(5)

(d) Torsional angles

A	B	C	D	Angle (°)
C(1)	Co(1)	Co(2)	C(2)	-155.86
C(1)	Co	C(3)	O(3)	19.00
C(1)	Co(1)	C(3)	O(4)	-179.79
C(2)	Co(2)	C(3)	O(3)	-177.69
C(2)	Co(2)	C(3)	O(4)	22.16
C(3)	C(4)	C(5)	C(6)	176.29
Cp(1)*	Co(1)	Co(2)	Cp(2)	127.08
C(1)	Co(1)	Co(2)	Cp(2)	-14.73
C(2)	Co(2)	Co(1)	Cp(1)	-14.05

* cp(1) and cp(2) represent the centroids of the cyclopentadienyl rings

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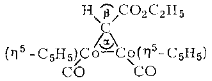
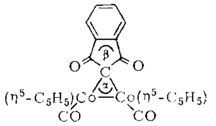
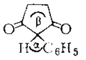
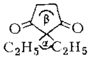
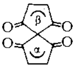
non-planarity of the methylene bridge is not unusual, nor is it induced by binding to the metals (*via* the methylidene bridge) since similar distortions from planarity have been observed in unbound indanediones listed in Table 4.

Table 4. Structural Parameters of the μ-Methylene Complexes **3** and **4** and Related Organic Methylene Compounds **5**-**7** (Angles [°], Distances [pm])

No.	**4**[2)	**3**	**5**[20)	**6**[21)	**7**[22)
					
α	80.4(1)	79.0(1)	–[a)	113.2(4)	104.0(3)
β	108 (2)	104.3(3)	103.0(6)	102.5(4)	103.8(3)
d (Co–Co)	249.5(1)	247.5(1)	–	–	–
d (Co–C)	194.7	194.5	–	–	174 [*d*(C–C)]

[a) Not given.

The Co – Co distance in complex **3** is similar to that reported earlier[2) for the ethoxycarbonylmethylene complex μ-$CH(CO_2C_2H_5)[(\eta^5-C_5H_5)Co(CO)]_2$ (**4**). In both cases, the Co – Co distance is approximately 15 pm longer than the value predicted from the addition of Pauling covalent radii[19) for two singly bonded cobalt atoms. Other similarities between **3** and **4** appear in the carbonyl distances, the methylene bonding parameters and the angles about the methylene bridge (Table 4). The internal angle Co(1) – C(3) – Co(2) (α) in the dioxoindanylidene complex **3** is substantially smaller than those found in other, purely organic, 1,3-indanediones. Using calculated distances[19) of 237 and 173 pm, respectively, for the Co – Co and Co – C bonds, one would predict an internal angle of 84.6° for both methylene bridged cobalt species. Both, in **3** and **4**, the internal angles are equal and smaller than the predicted value indicating that the bonding interaction between Co atoms is great enough to distort the Co – C – Co angle to a more acute value than that expected for a symmetrical, three-membered ring.

In examining the external angles β around the methylene carbon one finds that in **3** the value is smaller than that of the ideal tetrahedral result (tables 3 and 4). However, it should be noted that in the 1,3-dioxoindanylidene complex **3** there are geometrical constraints caused by the fusion of two rings at the methylene carbon. Thus, it is not surprising that the greatest similarities in these quantities occur between the title compound and the spiro compound **7** (Table 4). Note that while the external angles β remain constant for the compounds **5** – **7**[20–22) listed in table 4, the internal angles α change, supporting our earlier contention that correlations between the internal and external angles in methylene bridged species are difficult[2) because the values, thus observed, do not seem to be systematic. However, such lack of correlation between the values of α and β would not be surprising since *Ermer, Dunitz,* and *Bernal*[23) already demonstrated that there is no correlation at all between those angles in the case of organic methylene ($R^1 - CH_2 - R^2$) fragments.

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Experimental Part

The preparation of **3** was carried out in a dry nitrogen atmosphere. The solvents used were dried over Na/K-alloy (diethylether, benzene, pentane) or phosphorous pentoxide (dichloromethane). Elemental analyses were performed in the Mikroanalytisches Laboratorium der Universität Regensburg. Spectra: IR: Beckman Infrared Spectrophotometer 4220 with Data Processor 4060-A; ^{1}H NMR: Varian T60-A Spectrometer; Mass Spectra: Varian MAT CH 5 (direct inlet system).

1. *Preparation of μ-[1,3-Dioxoindane-2-ylidene]-bis[carbonyl(η⁵-cyclopentadienyl)cobalt]-(Co–Co)* (**3**): To a solution of 3.00 g (17 mmoles) dicarbonyl(η^5-cyclopentadienyl)cobalt (**1**)[24] in 70 ml benzene, 2.86 g (18 mmoles) 2-diazo-1,3-dioxoindane (**2**)[15] are added. When the dark red-brown solution is slowly heated to reflux, moderate gas evolution is observed which has ceased after ca. 8 h of refluxing the system. After the dark brown solution has been evaporated in a water aspirator, the oily residue is chromatographed on silica (Merck 7734; 0.063 – 0.200 mm; act. II – III; 45 × 1.8 cm; + 15°C). Unreacted **1** is chromatographed with benzene as eluent as quickly moving red band. The desired product **3** is developed with diethylether as a brown band. The solvent is stripped off in a water aspirator, and the brown, oily residue is dried in a high vacuum at room temperature and afterwards crystallized from a fairly concentrated diethylether solution at –35°C. The crystal used for the x-ray structure determination was grown from the same solvent by very slow temperature decrease down to –55°C. Brown to black-brown crystals, dec. above ca. 145°C (sealed capillary, heating speed 2°/min), complete decomposition at ca. 165°C. Yield 419 mg (11 %, based on **1**).

$C_{21}H_{14}Co_2O_4$ (448.2) Calc. C 56.28 H 3.15 Co 26.30 N 0.00
Found C 55.99 H 3.08 Co 26.19 N 0.02
Mol.-weight 448 (mass spectroscopically),
451 (osmometrically in chloroform)

2. *Crystallographically Important Data Collection and Data Processing Information*[25]

Empirical formula: $C_{21}H_{14}Co_2O_4$; molecular weight: 448.21 g · mole^{-1}; cell constants: a = 1033.6(15), b = 2258.5(21), c = 795.0(7) pm, β = 109.26(15)°; unit cell volume: 1751.84 · 10^6 pm^3; space group: *Cc*; density: (meas.) 1.698 gm · cm^{-3}, (calc. for $Z = 4$) 1.699 gm · cm^{-3}; radiation used for data collection: Mo-K_α ($\lambda = 0.71069$ Å); absorption coefficient (Mo-K_α): 19.14 cm^{-1}; scanning range for 2θ: $4.0° < 2\theta < 65.0°$; crystal along $[0\bar{1}\bar{1}]$; standards for intensity control (every 30 reflections): [392] and $[3\bar{9}2]$; scan width for each reflection: $\Delta\lambda = (0.85 + 0.35 \cdot \tan\theta)°$; maximum scan time: 5 min; prescan acceptance criterion[26]: $\sigma(I_{pre})/I_{pre} \leq 2.1$; scan technique: θ – 2θ; total number of reflections collected[27]: 3590; number of contributing reflections in the least-squares: 2699; number of variables: 298; weighting scheme: $w = 1/[\sigma^2(F) + 0.0026F^2]$; final $R(F)$[28]: 0.0310; final $R_w(F)$[29]: 0.0289.

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25) A list of the structure factors and a table of least squares planes are available upon request from one of the authors.

26) In the new CAD-4 software, the above criterion is used instead of a minimum number of counts on prescan.

27) A total of 3590 reflections were collected of which 2812 having $I > 2\sigma(I)$ were classified as „observed". Of those remaining, 119 systematic absences with non-zero intensities were removed prior to refinement.

28) $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$

29) $R_w(F) = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$, with $w = [\sigma^2(F_o) + 0.0026\,F_o^2]^{-2}$

[241/79]