Journal of Organometallic Chemistry, 165(1979)C17—C20

Preliminary communication

THE PREPARATION AND UNUSUAL REARRANGEMENT OF TRIPLY BRIDGED μ-HETEROMETHYLENECOBALT COMPLEXES. MOLECULAR STRUCTURE OF μ-ETHOXYCARBONYLMETHYLENEBIS[CARBONYL-(η^5-CYCLOPENTADIENYL)COBALT] (*Co—Co*)*

WOLFGANG A. HERRMANN*, ILONA SCHWEIZER,
Chemisches Institut der Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg 1 (Germany)
MICHAEL CRESWICK and IVAN BERNAL*
Chemistry Department, University of Houston, Houston/Texas 77004 (USA)

(Received September 29th, 1978)

Summary

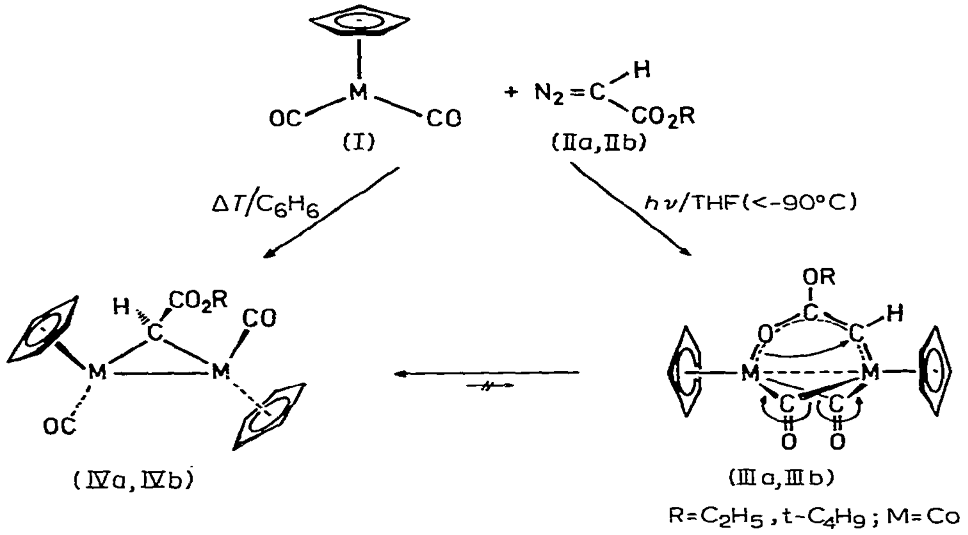
The μ-heteromethylenecobalt complexes, which have been synthesized by photolysis of (η^5-C_5H_5)Co(CO)$_2$ in the presence of the corresponding diazoacetates at < -90°C in tetrahydrofuran, undergo a novel type of intramolecular irreversible rearrangement yielding two isomers. The structure of one of the isomers has been established by X-ray analysis. A comparison of the structural parameters of all known μ-methylene-transition metal complexes shows that the internal angles α of the cyclopropane-like systems are far less sensitive to the compositions and structures of the molecules than the external angles β. The internal angles cannot be readily correlated with other features of the molecule.

We recently demonstrated that the thermal reactions of dicarbonyl(η^5-cyclopentadienyl)cobalt (I) with various dialkyl diazomalonates as well as alkyl diazoacetates (II) provide simple, high-yield syntheses of μ-methylene cobalt derivatives of type IV, which are not accessible by other means [2,3]. Upon photolysis of ethyl diazoacetate (IIa) or t-butyl diazoacetate (IIb), respectively, in the presence of I at < -90°C, however, along with the brown μ-methylene derivatives IVa and IVb we obtained also the green, crystalline compounds IIIa and IIIb**, which have been shown by elemental analysis, mass spectra, IR and

---

*Transition metal methylene complexes. V, for part IV see ref. 1; also Studies on metal-metal bonds, IV, for part III see ref. 2.

**For experimental, spectroscopic and kinetic details see ref. 3. Elemental analyses. IIIa: Found: C, 49.52; H, 4.26; Co, 30.18; N, 0.00; O, 16,58; molecular weight 390 (mass spectr.). $C_{16}H_{16}Co_2O_4$ calcd.: C, 49.26; H, 4.13; Co, 30.21; N, 0.00; O, 16.41%; molecular weight 390.2. IIIb: Found: C, 51.69; H, 4.82; Co, 28.18; N, 0.00; molecular weight 418 (mass spectr.). $C_{18}H_{20}Co_2O_4$ calcd.: C, 51.70; H, 4.82; Co, 28.18; N, 0.00%; molecular weight 418.2.



^{1}H NMR spectra to be isomers of IVa and IVb, respectively. Although the triply bridged low-temperature products IIIa and IIIb are thermally stable in the solid state, they undergo an interesting irreversible rearrangement in solution. The dark-green solutions of IIIa and IIIb in methylene chloride rapidly turn brown at ambient temperature without decomposition. The products formed during these isomerizations are identical with the known [1] μ-methylene complexes IVa and IVb, respectively, which can be isolated pure without further purification. By means of IR and ^{1}H NMR techniques we characterized both the carbonyl bridge opening and the μ-methylene rearrangement as intramolecular processes. This hitherto unknown type of isomerization (IIIa → IVa, IIIb → IVb) strictly obeys a first order rate law (e.g. process IIIa → IVa at T 290.5 ± 2 K: $k = (3.80 \pm 0.03) \times 10^{-4}$ sec^{-1}; $\tau_{1/2} = 30.37 \pm 0.24$ min; $\Delta G^{\ddagger} = 21.54 \pm 0.20$ kcal degree^{-1} mol^{-1}; CH_2Cl_2). The reverse of the rearrangements presented here has not been achieved by any means. The identity of the isomerization products has also been proved by an X-ray analysis performed on the ethyl derivative IVa*. Figure 1 shows the molecule, which is characterized by the following structural parameters:

Bond lengths (pm)	
Co(1)—Co(2)	249.5(1)
Co(1)—C(3)	195.1(6)
Co(2)—C(3)	194.4(7)
Av. Co—C(O)	170.8

Bond angles (°)	
Co(1)—C(3)—Co(2)	79.6(2)
Co(1)—Co(2)—C(3)	50.3(2)
Co(2)—Co(1)—C(3)	50.1(2)
C(4)—C(3)—H(4)	92.6(2)

Torsional angle (°)	
C(1)—Co(1)—Co(2)—C(2)	−159.80

---

*Enraf Nonius CAD-4 (Mo-K_α). Space group: $P2_1$ with a 729.9(2), b 785.9(2), c 2723.7(4) pm, β 91.74(2)°, Z 4. A total of 3215 reflections were collected of which 2069 had $I > 3\sigma(I)$ and were used in the solution and refinement. R(F) 2.97%, $R_w(F)$ 2.60%. For crystallographic details see ref. 5.

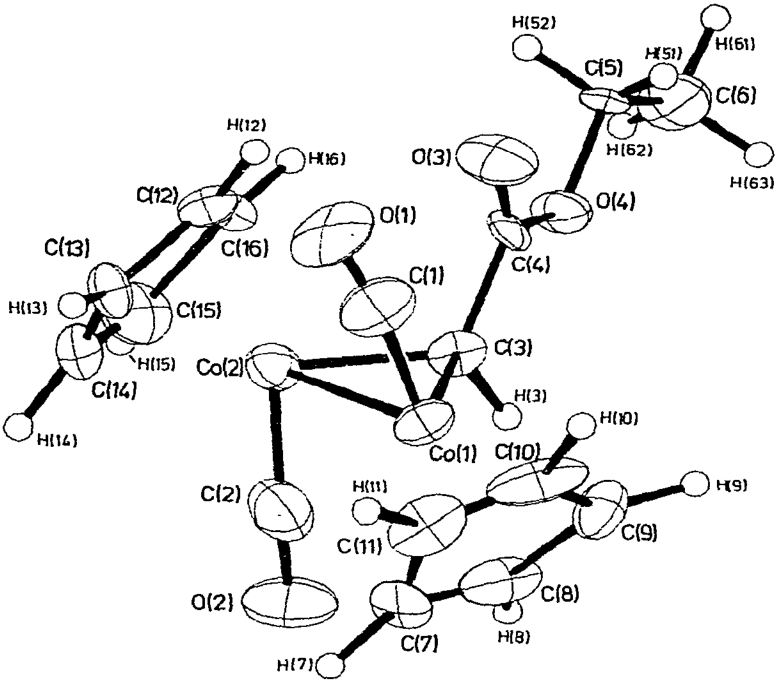
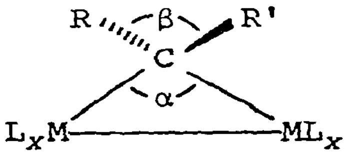


Fig. 1.

It is of interest to note that the Co—Co distance in this molecule has a value which is closer to those found in the compounds described as Class A and Class B of tetra-bonded dinuclear cobalt complexes, than to those in Class C, which are formally three-bonded [6]. Thus, a metal—metal bond and the bridging methylene seem to take the place of the two bridging carbonyl ligands present in the entire set of compounds we listed as Classes A and B in our previous paper [6]. This remarkable observation is not unique to this Co—Co dimer, having been observed (but not discussed) in the case of μ-$CH_2[\eta^5$-$C_5H_5)Rh(CO)]_2$ [2]. Furthermore, the same result is obtained in the analogous binuclear cobalt complex in which the ethoxycarbonylmethylene bridge of IVa is replaced by 1,3-dioxoindaneylidene(2) [7b]. Finally, for the class of compounds containing bridging methylenes [1,2,7] the internal angle α is much less sensitive than the external angle β to changes in such variables as (a) the pair of metals involved,



(b) the length of the metal—metal bond, and (c) the nature of the substituents R and R′ bound to the methylene carbon (see Table 1). Such changes in the internal angle α cannot be readily correlated with (1) changes in the external angle β, (2) the nature of the groups R and R′ (i.e. steric effects, such as crowding, are not logically related to variations in α or β), (3) the length of the metal—metal bond, nor (4) obvious features of the metals themselves, such as the number of d-electrons.

TABLE 1

INTERNAL ANGLES α [°] AND EXTERNAL ANGLES β [°] OF μ-METHYLENE LIGANDS

ML_x	R	R′	Number of bridging ligands	α	β	Reference
$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2$	H	H	1	86.9(2)	92(2)	7a
$(\eta^5\text{-}C_5H_5)Rh(CO)$	H	H	1	81.7(1)	115.9(4)	2,4
$(\eta^5\text{-}C_5H_5)Rh$[a]	C_6H_5	C_6H_5	3	75	[f]	7c
$(\eta^5\text{-}C_5H_5)Rh$[b]	C_6H_5	C_6H_5	2	≈76[g]	[f]	7c
$(\eta^5\text{-}C_5H_5)Co(CO)$	H	$CO_2C_2H_5$	1	79.6(2)	92.6(2)	*this work*
$(\eta^5\text{-}C_5H_5)Co(CO)$	1,3-dioxoindaneylidene(2)		1	79.0(1)	104.3(3)	7b
$Co(CO)_3$[c]	OC(=O)CH=CH		2	75	108	7d
$Ru[P(CH_3)_3]_3$[d]	H	H	3	≈78	[f]	7e
$Re(CO)_4$[e]	OCH_3	$C_6H_4CH_3\text{-}p$	2	77(1)	115(3)	7f
$Fe(CO)_3$	Carbocyclic ligand	$C_7H_8\text{-}\mu\text{-}$alkylidene	2	81.4	[f]	7g

[a] $[\mu\text{-}C(C_6H_5)_2]_2\text{-}\mu\text{-}CO[(\eta^5\text{-}C_5H_5)Rh]_2$. [b] $[\mu\text{-}C(C_6H_5)_2]_2[(\eta^5\text{-}C_5H_5)Rh]_2$. [c] $[\mu\text{-}C_4H_2O_2]\text{-}\mu\text{-}CO[Co(CO)_3]_2$. [d] $(\mu\text{-}CH_2)_3\{Ru[P(CH_3)_3]_3\}_2$. [e] $[\mu\text{-}C(OCH_3)(C_6H_4CH_3\text{-}p)]_2[Re(CO)_4]_2$. [f] Not given. [g] No exact figures given.

Acknowledgement

This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the US National Science Foundation and the Welch Foundation.

References

1 W.A. Herrmann, Chem. Ber., 111 (1978) 1077.

2 W.A. Herrmann, C. Krüger, R. Goddard and I. Bernal, J. Organometal. Chem., 140 (1977) 73.

3 W.A. Herrmann and I. Schweizer, Z. Naturforsch., in preparation.

4 W.A. Herrmann, C. Krüger, R. Goddard and I. Bernal, Angew. Chem. Intern. Edit. Engl., 16 (1977) 334.

5 I. Bernal et al., Inorg. Chem., in preparation.

6 I. Bernal, J.D. Korp, G.M. Reisner and W.A. Herrmann, J. Organometal. Chem., 139 (1977) 321.

7 (a) I. Bernal, M. Creswick and W.A. Herrmann, Angew. Chem. Intern. Edit. Engl., in preparation; quoted in: W.A. Herrmann, Angew. Chem. Intern. Edit. Engl., 17 (1978) in press; (b) M. Creswick, I. Bernal, W.A. Herrmann and I. Steffl, Chem. Ber., in press; (c) H. Ueda, Y. Kai, N. Yasuoka and N. Kasai, 21th Symp. Organometal. Chem., Sendai/Japan (Oct. 4—6, 1973), Abstr. p. 214; (d) O.S. Mills and G. Robinson, Inorg. Chim. Acta, 1 (1967) 61; (e) R. Anderson, R.A. Jones, G. Wilkinson, M.B. Hursthouse and K.M. Abdul Malik, J. Chem. Soc. Chem. Commun., (1977) 865; (f) E.O. Fischer, T.L. Lindner, H. Fischer, G. Huttner, P. Friedrich and F.R. Kreissl, Z. Naturforsch. B, 32 (1977) 648; (g) R. Aumann, H. Wormann and C. Krüger, Angew. Chem. Intern. Edit. Engl., 15 (1976) 609.