

A Cobalt-Cobalt Bond Supported by Bridging Tin and Carbonyl Groups

By D. J. PATMORE and W. A. G. GRAHAM

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada)

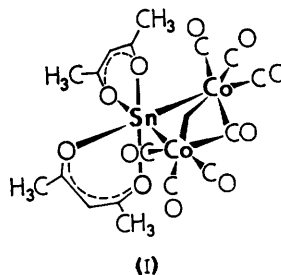
NUMEROUS compounds have been reported in which tetracarbonylcobalt groups are bonded to four-coordinate tin: $\text{Ph}_3\text{SnCo}(\text{CO})_4$,¹ $\text{Cl}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$,² and $\text{MeSn}[\text{Co}(\text{CO})_4]_3$ ³ will serve as examples. We now report a cobalt carbonyl derivative of six-coordinate tin with some novel structural features.

Reaction of bis(acetylacetonato)dichlorotin(IV) with tetracarbonylcobalt(-I) anion affords a moderately stable red crystalline compound, m.p. 86–88° (decomp.). Analysis indicates a composition $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$, and this formula is confirmed by an exact mass determination on the 632 peak of the mass spectrum. In cyclohexane, the infrared spectrum shows terminal carbonyl stretching bands at 2076 (m), 2036 (s), 2013 (s), 2004 (m), and 1994 (m) cm^{-1} , and one band at 1836 (m) cm^{-1} which can be ascribed to a bridging carbonyl group. Several bands in the 1500–1600 cm^{-1} region can be assigned to $(\text{C}=\text{O})$ and $(\text{C}=\text{C})$ in the acetylacetonato-rings.⁴ The compound is essentially diamagnetic.

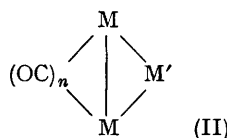
On the above evidence, we suggest structure (I) for the compound. A cobalt-cobalt bond is required to preserve the inert-gas configuration for the cobalt atoms, and we represent this bond as "bent" to suggest an octahedral geometry around the cobalt atoms. The formation of (I) can be regarded as a displacement of chloride ions from $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCl}_2$ (which most probably has the *cis*-configuration⁵) to give *cis*- $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$. Spontaneous loss of CO and Co-Co bond formation then lock the molecule in the *cis*-form.

Isolation of such a compound supports our suggestion³ that similar bridged species are formed readily in the mass spectrometer from $\text{XSn}[\text{Co}(\text{CO})_4]_3$ and $\text{X}_2[\text{Co}(\text{CO})_4]_2$; for these molecules, the molecular ion was not detected, and the most abundant ion was lighter by one CO group. Under ordinary conditions, these derivatives of four-coordinate tin do not lose CO, presumably because

the Co-Sn-Co bond angle is larger than in the six-coordinate compound (I).



Structure (I) can be derived from that of cobalt carbonyl by replacing one bridging CO with the $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}$ group; from this point of view it is related to the carbon-bridged structure of $\text{Co}_2(\text{CO})_9\text{HC}\equiv\text{CH}$.⁶ In relation to the general structural type represented by (II) (M, M' metal



atoms, n the number of bridging CO groups), compound (I) is believed to provide the first example with $n = 1$. Examples in which $n = 0$ are $\text{Os}_3(\text{CO})_{12}$,⁷ and a novel compound with $\text{M} = \text{Fe}$ and $\text{M}' = \text{Sn}$.⁸ The solid-state structure⁹ of $\text{Fe}_3(\text{CO})_{12}$ is representative of (II) where $n = 2$, while a related heterocyclic case ($\text{M} = \text{Fe}$, $\text{M}' = \text{Mn}$) is considered to be present in the anion $[\text{MnFe}_2(\text{CO})_{12}]^-$.¹⁰

(Received, November 8th, 1966; Com. 868.)

¹ F. Hein and W. Jehn, *Annalen*, 1965, 684, 4.

² D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, 5, 1405; F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc. (A)*, 1966, 1052.

³ D. J. Patmore and W. A. G. Graham, *Inorg. Nuclear Chem. Letters*, 1966, 2, 179; *Inorg. Chem.*, in the press.

⁴ K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 216.

⁵ J. A. S. Smith and E. J. Wilkins, *Chem. Comm.*, 1965, 381.

⁶ O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 1959, 156.

⁷ E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, 1, 521.

⁸ J. D. Cotton, J. Duckworth, S. A. R. Knox, P. F. Lindley, I. Paul, F. G. A. Stone, and P. Woodward, *Chem. Comm.*, 1966, 253.

⁹ C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, 88, 1821.

¹⁰ U. Anders and W. A. G. Graham, *Chem. Comm.*, 1966, 291.