

*Neutralization of an aqueous solution of Zeise's salt in presence of amino acid hydrochloride.* This method was useful only in the case of  $\beta$ -phenylalanine. To a cold solution of 2.1 g (5.4 mmole) of potassium trichloro(ethylene)platinum(II) in 12 ml of water was added a solution of 0.89 g (5.4 mmole) of DL- $\beta$ -phenylalanine in 15 ml of 0.5 N HCl. Cooled 1 N KOH was added, under cooling and stirring, until a pH of 6.5 was reached. The temperature of the mixture was then raised to 45°. After a few minutes the complex separated, as well-formed yellow needles (2.11 g, 93%).

*Reaction of Zeise's salt and the amino acid in water.* In the conditions tried by us, this method was the least useful. As an example, a solution of 0.33 g (2 mmole) of DL- $\beta$ -phenylalanine was added to a solution of 0.77 g (2 mmole) of potassium trichloro(ethylene)platinate(II) in 5 ml of the same solvent. After 3 h at room temperature 0.16 g (19%) of the complex separated.

Centro Nazionale di Chimica  
delle Macromolecole del C.N.R.,  
Sez. VII, Università di Napoli,  
Via Mezzocannone 4, Napoli (Italy)

ACHILLE PANUNZI  
ROSARIO PALUMBO  
CARLO PEDONE  
GASTONE PAIARO

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## A novel transition-metal silicon carbonyl, and the bonding in $\text{Co}_3(\text{CO})_9\text{R}$ molecules

The nature of the bonding within molecules containing a tetrahedron<sup>1</sup> or equilateral triangular array<sup>2</sup> of metal atoms has recently been discussed in terms of equivalent orbitals. In the present paper we use the same approach to discuss the electronic structure of a series of compounds which have structures intermediate between these two geometries. In molecules with the general formula  $\text{Co}_3(\text{CO})_9\text{R}$  three cobalt atoms lie at the corners of an equilateral triangle and the R group completes the tetrahedron (Fig. 1). Compounds with a variety of substituent R have been prepared. Dent *et al.*<sup>3</sup> prepared a number with  $\text{R} = \text{CR}'$ , we have reported elsewhere<sup>4</sup> that with  $\text{R} = \text{Si}-\text{CH}=\text{CH}_2$  and more recently the compound with  $\text{R} = \text{Sn}-\text{Bu}$  has been described<sup>5</sup>.

It appears that there are generally nine metal-metal bonding molecular orbitals in an equilateral triangular array of transition metal ions. Three of these, of  $A + E$  symmetry (in  $C_{3v}$ ), are symmetric with respect to reflection in the plane of the triangle, the corresponding equivalent orbitals being metal-metal bent  $\sigma$  orbitals. The other six may also be considered to be derived from localized metal-metal bonds, three on either side of the metal triangle. In the case of  $\text{Co}_3(\text{CO})_9\text{R}$  molecules the three

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out of plane bonds on one side of the triangle interact with three orbitals of the R group, one of  $A_1$  and a pair of  $E$  symmetry. From a detailed consideration of a general  $M(CO)_3$  group, where M is a transition metal, it appears likely that two metal orbitals are largely involved in back-bonding with the three carbonyl groups<sup>6</sup>. This conclusion

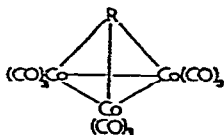


Fig. 1.

finds support in work on the electronic structure of metal tetrahedra where four electrons on each metal atom are frequently involved in extra-tetrahedron  $\pi$  bonding<sup>1</sup>. We conclude that there are a total of fifteen bonding orbitals to be filled in the  $Co_3(CO)_9R$  structure. There are thirty electrons available (seven valence electrons from each cobalt and three from the R group) which just fill the available orbitals.

Bor, Marko and Marko<sup>7</sup> have reported the preparation of the compound  $[Co_3(CO)_9C]_2$  which is unusual in that two metal carbonyl fragments are joined by what is formally a carbon-carbon single bond. It seems most probable that this molecule retains a threefold rotation axis<sup>7</sup>. If this is so it strongly suggests that the C-C bond has, in fact, appreciable multiple bond character.

We now report the preparation of a silicon compound analogous to that reported by Bor, Marko and Marko,  $[Co_3(CO)_9Si]_2$ . This compound was made in low yield by refluxing dicobalt octacarbonyl with tetraphenylsilane in petroleum ether. It is soluble in most organic solvents and sublimes *in vacuo* at ca.  $45^\circ$  to give a violet crystalline sublimate. The compound is stable in air if refrigerated and remains unchanged indefinitely if stored under nitrogen. This compound is the first metal carbonyl to be prepared which contains a Si-Si bond. It appears that Si-Si single bond energy is comparable to the C-C single bond energy<sup>8,9</sup> so the comparable stability of  $[Co_3(CO)_9Si]_2$  and  $[Co_3(CO)_9C]_2$  may be indicative of multiple bond character in the former. It is tempting to suggest that silicon  $d$  orbitals are involved, and, indeed, there are orbitals of the correct symmetry and orientation to overlap with them within the cobalt triangle. However, the visible spectrum of the silicon compound is similar to those of members of the carbon series, as is also the infra-red spectrum, unlike that of vinylsilicon tricobalt nonacarbonyl.

### Experimental

A solution of dicobalt octacarbonyl (3.1 g) and tetraphenylsilane (2.9 g) was refluxed in low boiling petroleum ether (60 ml) for 2.5 h under nitrogen. The solution was centrifuged and then chromatographed on alumina eluting with petroleum ether. Unchanged reactants were rapidly eluted from the column leaving a reddish-brown band. This was extracted with carbon tetrachloride to give a reddish-brown solution. After removal of the solvent and vacuum sublimation, the impure product was obtained. It was purified by alumina chromatography using carbon tetrachloride as eluant, removal of solvent and resublimation. (Found: C, 23.2; H, 0.7; Co, 37.8; CO, 54.2.  $C_{18}O_{18}Co_9Si_2$  calcd.: C, 23.6; Co, 38.7; CO, 55.1 %.) The compound is diamagnetic; a proton resonance spectrum of a concentrated solution in carbon tetra-

chloride showed no absorption. The infrared spectrum, recorded as a carbon tetrachloride solution on a Unicam S.P. 100 spectrometer, showed terminal carbonyl absorption at 2112 (s), 2065 (s), 2048 (s), 2032 (w) and 1992 (w)  $\text{cm}^{-1}$ .

*Department of Chemistry, The University,  
Sheffield 10 (England)*

S. F. A. KETTLE  
IRSHAD A. KHAN\*

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\* Present address: Department of Chemistry, University of Karachi, Karachi 32, West Pakistan.

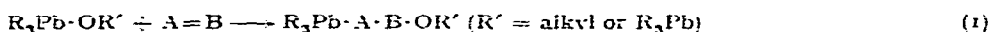
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## PRELIMINARY NOTES

### Addition reactions of the lead-oxygen bond.

#### Routes to trichloromethyltriphenyllead and tribromomethyltriphenyllead

Organotin alkoxides and oxides add to many types of multiply-bonded acceptor molecules, providing the basis for new organic and organometallic syntheses<sup>1</sup>. Similar reactions (equation 1) have now been established for organolead compounds.



Triphenyllead methoxide (m.p. 89-90°; from triphenyllead chloride and sodium methoxide in benzene), tributyllead methoxide (m.p. 46-48°; from the chloride and sodium methoxide in ether), and bistriphenyllead oxide react rapidly and usually exothermically at room temperature with the acceptor molecules shown in the first column of Table 1. The adducts listed in the second column have been isolated with satisfactory analyses.

In the few cases where the reactions are slow enough to allow a comparison to be made, the lead-oxygen bond is clearly more reactive than the corresponding tin-oxygen bond<sup>1,2</sup>. The adducts containing the triphenyllead group are stable under nitrogen, but those with the tributyllead group are thermally or photolytically un-

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