*Journal of Organometallic Chemistry*, 226 (1984) C8—C10
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**Preliminary communication**

# INSERTION OF THE $Pt(PPh_3)_2$ UNIT INTO INORGANIC TRIATOMIC RINGS COORDINATED TO METAL—LIGAND MOIETIES

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(Received December 21st, 1983)

## Summary

Reaction of the $[(triphos)Co(E_2S)]BF_4$ complexes (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, E = P or As) containing the $P_2S$ or $As_2S$ cyclic units *trihapto*($\eta^3$)-bonded to the metal, with $(C_2H_4)Pt(PPh_3)_2$ involves insertion of the $Pt(PPh_3)_2$ moiety into a bond of the inorganic ring, yielding the compounds $[(triphos)Co(E_2S)Pt(PPh_3)_2]BPh_4$ (E = P or As), whose structures have been determined by X-ray diffraction studies.

We recently found that cobalt complexes containing the heterocyclic diphosphorus sulphur or diarsenic sulphur units *trihapto*($\eta^3$)-coordinated to the metal atom are obtained by reaction of cobalt salts with tetraphosphorus or tetraarsenic trisulphide in presence of the ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $MeC(CH_2PPh_2)_3$(triphos) [1—3]. During investigations of the reactivity of such coordinated inorganic rings we have found that on reaction of the $[(triphos)Co(E_2S)]BF_4$ (E = P, As) complexes with $(C_2H_4)Pt(PPh_3)_2$ insertion of the $Pt(PPh_3)_2$ unit into a bond of the $E_2S$ ring occurs. Although this bond lengthens considerably, involving a large distortion of the triatomic group, each of the $E_2S$ atoms remains coordinated to the cobalt atom. To our knowledge, no reaction of this type has been previously reported for complexes formed by triatomic inorganic rings. In particular, the geometry of the homocyclic $P_3$ group in the cyclo-triphosphorus complexes has previously been found to be substantially unaffected by transformations involving the parent compounds [4,5].

The compounds $[(triphos)Co(E_2S)Pt(PPh_3)_2]BPh_4$ (E = P or As), were obtained by reaction of acetone solutions of $(C_2H_4)Pt(PPh_3)_2$ and $[(triphos)Co(E_2S)]BF_4$ (E = P, As) under nitrogen. After addition of $NaBPh_4$ dissolved in ethanol red-brown crystals of the compounds were obtained by concentrating

0022-328X/84/$03.00

the resulting solution. C, H, As, Co, P and S elemental analyses agreed with the above formula. The compounds are moderately air sensitive both in the solid state and in solution. The structures of the two compounds, which are isomorphous with each other, have been established by single-crystal X-ray diffraction studies and details for the $As_2S$ derivative are reported here.

*Crystal data*: $C_{101}H_{89}As_2BCoP_5PtS$, $M = 1904.44$, monoclinic, $a$ 19.298(10), $b$ 21.900(12), $c$ 10.187(8) Å, $\beta$ 98.37(9)°, $U$ 4259.4 Å$^3$, space group $P2_1$, $Z = 2$, $D_c$ 1.484 g cm$^{-3}$, $F(000)$ 1924 electrons, $\mu$(Mo-$K_\alpha$) 27.83 cm$^{-1}$. Intensity data were collected on a Philips PW 1100 diffractometer using Mo-$K_\alpha$ ($\lambda$ 0.71069 Å) radiation. 2952 reflections with $I \geqslant 3\sigma(I)$ were used to solve (Patterson and Fourier methods) and refine (full matrix least-squares; Pt, Co, As, S anisotropic, Ph rigid groups, H in calculated positions) the structure to $R$ of 0.044. The occupancy factors for the three sites of the $As_2S$ group, which is affected by dis-

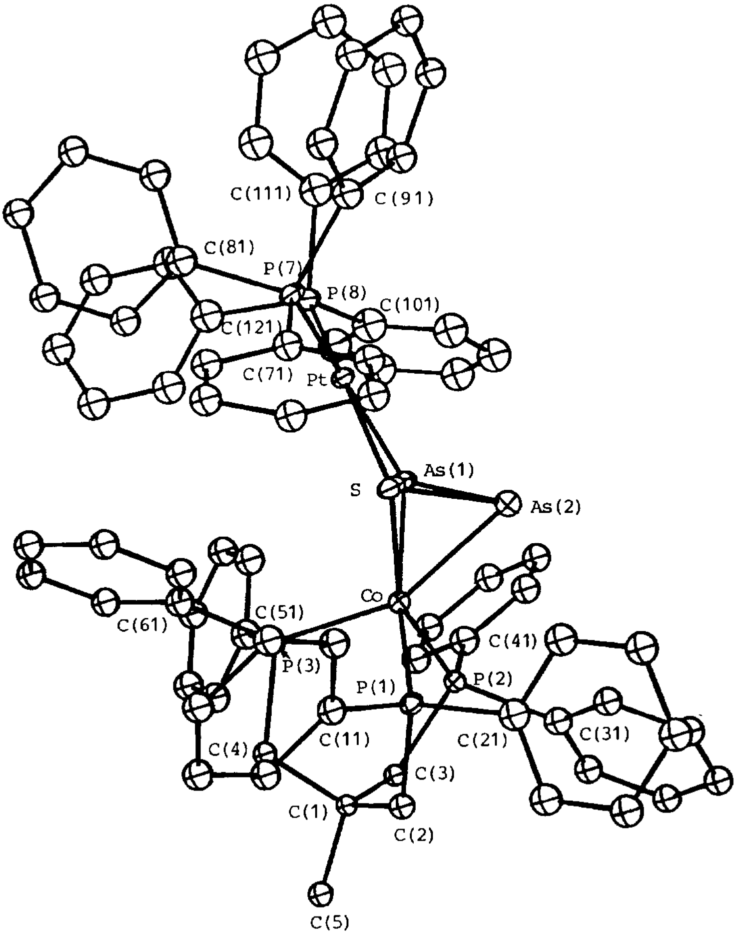

Fig. 1. A view of the $[(triphos)Co(As_2S)Pt(PPh_3)_2]^+$ cation. The occupancies of sites in the $As_2S$ ring are: As(1) (0.56 As, 0.44 S), As(2) (1.00 As, 0.00 S), S (0.44 As, 0.56 S). Bond distances: As(1)—S 3.03(1), As(1)—As(2) 2.35(1), As(2)—S 2.35(1), Co—P(1—3) 2.21—2.26, Co—As(1) 2.45(1), Co—As(2) 2.36(1), Co—S 2.42(1), Pt—As(1) 2.47(1), Pt—S 2.43(1), Pt—P(4), 2.33(1), Pt—P(5) 2.35(1) Å. Bond angles: As(1)—Co—S 77.2(1), As(1)—Co—As(2) 58.6(1), As(2)—Co—S 58.8(1), As(1)—As(2)—S 80.4(1), As(1)—Pt—S 76.5(1), P(4)—Pt—P(5),101.6(2)°.

order, were refined by assuming that values of the equivalent isotropic temperature factors must be similar for the three sites. The site not bound to Pt was finally considered to be occupied only by As, since the temperature factor became too low upon assignment of even small fractions (<10%) of S character. The S atom was found to be almost equally distributed between the two sites linked to Pt*.

The structure of the $As_2S$ derivative consists of $[(triphos)Co(As_2S)Pt(PPh_3)_2]^+$ cations and $BPh_4^-$ anions. The cobalt atom is coordinated by the three phosphorus atoms of the triphos ligand (Fig. 1) and by the atoms of the $As_2S$ unit. The latter is considerably distorted from the regular triangular shape it has in the parent $[(triphos)Co(As_2S)]^+$ cation [3] since the bond in which insertion of the $Pt(PPh_3)_2$ moiety occurs lengthens to 3.03(1) Å, whereas the other two bond distances average to 2.35(1) Å (corresponding values are 2.81(1) and 2.15(1) Å for the isomorphous $P_2S$ derivative). The platinum atom is in a nearly planar arrangement formed by the two $PPh_3$ phosphorus atoms and by the two atoms defining the long side of the distorted $As_2S$ group. Insertion of the $Pt(PPh_3)_2$ moiety is considered to take place into one of the heteroatomic As—S bonds rather than on the As—As bond in the ring on the basis of the refinement of the occupancy factors of the sites in the bridging $As_2S$ group. In the case of the $P_2S$ derivative insertion is also considered to involve one of the heteroatomic P—S bonds since the $^{31}P$ NMR spectrum of the compound exhibits two signals (−121.7 and −131.0 ppm; $H_3PO_4$ 0.0 ppm) for the phosphorus atoms of the $P_2S$ unit, which are therefore non-equivalent. Values of important bond distances and angles in the structure of the $As_2S$ derivative are given in the caption. The dihedral angle between the plane of the triatomic unit and the least squares plane through the four atoms surrounding Pt is 52°.

**Acknowledgement.** We thank Prof. L. Sacconi for his interest in this work. Financial support from Italian C.N.R. under the "Progetto Finalizzato Chimica Fine e Secondaria" is gratefully acknowledged.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.