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Preliminary communication

SYNTHESIS OF ZEROVALENT TRIS[BIS(1,2-(DIMETHYLPHOSPHINO)-ETHANE] COMPOUNDS OF CHROMIUM, MOLYBDENUM, TUNGSTEN, VANADIUM, NIOBIUM AND TANTALUM USING THE METAL VAPOURS

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Summary

Cocondensation of the vapours of the metals Cr, Mo, W, V, Nb and Ta, with an excess of dmpe (bis(dimethylphosphino)ethane) gives the neutral, zerovalent compounds M(dmpe)$_3$; the compound Ta(dmpe)$_3$ is the first example of a zerovalent derivative of tantalum.

The compounds M(dmpe)$_3$ where M = Cr, Mo, W or V have been prepared by Chatt and Watson [1] by reduction of the metal halides in the presence of an excess of dmpe.

We were interested to discover whether these and related compounds could also be prepared by direct condensation of the metal atoms with an excess of the dmpe and, if so, to study their structures and reactions.

We have found that condensation of vapours of the metals M = Cr, Mo, W, V, Nb and Ta generated from an electron gun furnace operating at a positive potential [2] with dmpe gives excellent yields of the neutral compounds M(dmpe)$_3$.

In a typical experiment, niobium (0.21 g) was evaporated from a molten ingot (5 g) at 3000°C over a period of 2 h and the vapour was cocondensed with an excess of dmpe (25 cm^3). Relatively little unreacted metal was observed in the reaction mixture after warming to room temperature, yields based on metal leaving the furnace were >55%, i.e. 2.0 g of Nb(dmpe)$_3$; 0.5 g of vanadium lead to 3 g of V(dmpe)$_3$ in the same condition, yield >60%.

The new compounds where M = Nb or Ta represent rare examples of zerovalent derivatives of these metals; they are dark red and very sensitive to air and water. Satisfactory microanalysis have been obtained and the mass spectra show parent ion bands at m/e 543 (^{93}Nb) and 631 (^{181}Ta). (ESR data at 77 K in

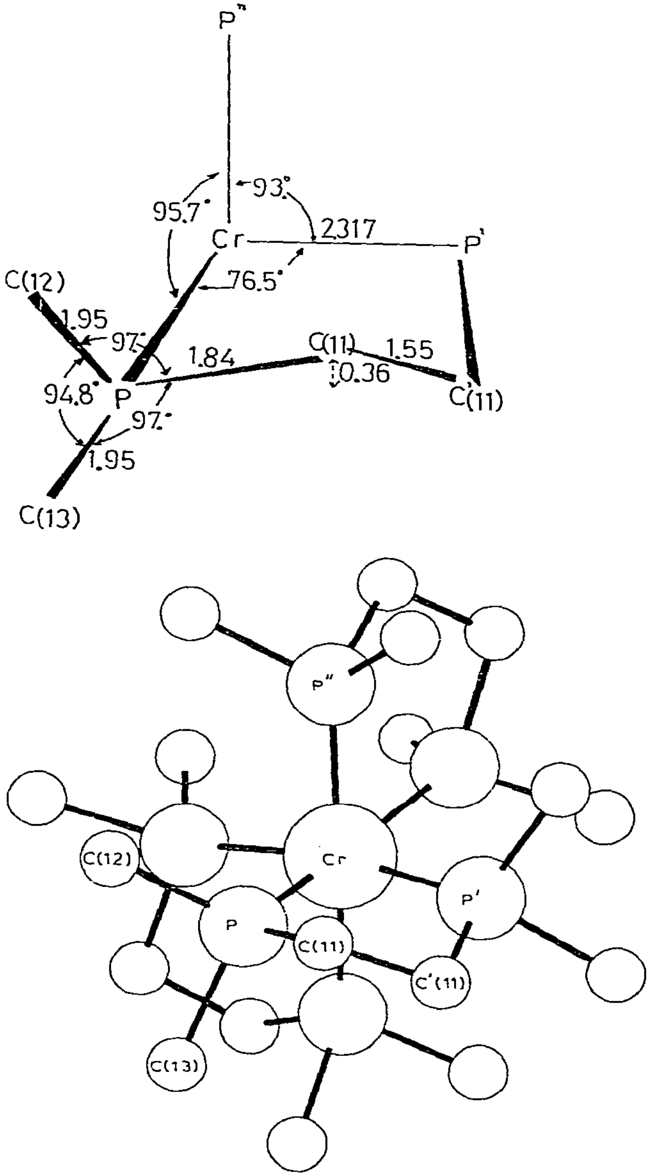

Fig. 1. (a) Distances (Å) and angles (°) for the Cr(dmpe) fragment; (b) crystal structure of Cr(dmpe)$_3$.

toluene: M = V: 15 lines approximatively symmetrical in distribution; M = Nb; 29 lines in a complex band of irregular shape; M = Ta: a single very broad band of irregular shape). The ESR data are consistent with the paramagnetism expected for the compounds where M = V, Nb and Ta.

We have obtained single crystals of each compound. The unit cells of the six crystals are cubic and the variations of the dimension of these cells are in full agreement with the expected values.

$$\begin{tikzcd}
\text{V (11.041(3) Å)} \arrow[r, "-0.119\text{ Å}"] \arrow[d, "+0.153\text{ Å}"] & \text{Cr (10.922(3) Å)} \arrow[d, "+0.136\text{ Å}"] \\
\text{Nb (11.194(4) Å)} \arrow[r, "-0.136\text{ Å}"] \arrow[d, "-0.030\text{ Å}"] & \text{Mo (11.058(5) Å)} \arrow[d, "-0.018\text{ Å}"] \\
\text{Ta (11.164(3) Å)} \arrow[r, "-0.124\text{ Å}"] & \text{W (11.040(5) Å)}
\end{tikzcd}$$

The crystal structure of the Cr(dmpe)$_3$ has already been established; the structures of the five other compounds will be published later.

Crystal data: $C_{18}H_{48}CrP_6$, M 502.5 g/mol, cubic, a 10.922(3) Å, space group $Im3m$ (from Laüe symmetry, systematic absences and structure analysis), $Z = 2$, $D_{\text{calc.}}$ 1.28 g cm^{-3}, 166 independent reflections with $I > 3\sigma$ were measured by four-circle diffractometer using Mo-K_α radiation (0.71069 Å).

The Cr(dmpe)$_3$ molecule has point symmetry 32 but the symmetry of the only possible crystallographic site of the Cr atom is $m3m$. Thus each molecule will occupy one of 8 possible sites with symmetry 32 so that the average of the distribution has the symmetry $m3m$.

The Patterson function suggested that the phosphorus atoms were on four-fold axis but an electron density difference synthesis indicated that these atoms were located in general position close to the axes. The carbon atoms were then placed and refinement of the 38 parameters was carried out using the disordered model with various Waser [3] constraints. The conventional agreement index R is now 0.04.

The chromium atom is at the center of a distorted coordination octahedron. The phosphorus atoms are at a distance of 2.317(3) Å from the chromium, at 1.84(3) Å, 1.95(4) Å and 1.95(5) Å, respectively, from the carbon atoms C(11), C(12) and C(13). The atom C(11) is 0.36 Å above the plane defined by P(1), P'(1) and Cr and at a distance of 1.55(6) Å from the carbon atom symmetrical with the respect of the two-fold axis. The angle P(1)—Cr—P'(1) within a chelate ring is 76.5(3)°, P(1)—Cr—P''(1) and P'(1)—Cr—P''(1) are respectively 95.7(7)° and 93(1)° (Fig. 1).

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References

1 J. Chatt and H.R. Watson, J. Chem. Soc., (1962) 1343.
2 M.L.H. Green, J. Organometal. Chem., 200 (1980) 119.
3 J. Waser, Acta Cryst., 16 (1963) 1091.