# Synthesis, and Crystal and Molecular Structure of μ-Dibromo-μ-tetraphenyldiphosphane-bis[tricarbonylrhenium(I)], a Molecule Containing a New Type of Tetraphenyldiphosphane Bridge

By JERRY L. ATWOOD,* J. KAY NEWELL, and WILLIAM E. HUNTER
(*Department of Chemistry, University of Alabama* 35486)

IVAN BERNAL
(*Department of Chemistry, University of Houston, Houston, Texas* 77004)

and FAUSTO CALDERAZZO,* ISHWERLAL P. MAVANI, and DARIO VITALI
(*Istituto Chemica Generale, University of Pisa,* 56100 *Pisa, Italy*)

*Summary* No cleavage of the P–P bond occurs during the reaction of the tetrahydrofuran (thf) complex $[Re_2Br_2(CO)_6(thf)_2]$ with $P_2Ph_4$ in toluene; an *X*-ray study shows that the resulting compound contains bridging tetraphenyldiphosphane in a unique type of bonding.

REACTIONS of low-valent transition metal complexes with dialkyl- and diaryl-disulphanes, and tetra-alkyl- and tetra-aryl-diphosphanes often result in oxidative addition across the S–S[1] or P–P[2] bond with formation of the corresponding SR- or $PR_2$-bridged dinuclear or polynuclear species. However, previous work had shown that the reaction[3] of $S_2Ph_2$ with $[Re_2Br_2(CO)_6(thf)_2]$[4] (thf = tetrahydrofuran) does not lead to S–S bond cleavage and a dimer containing both Br and $S_2Ph_2$ bridges[5] was obtained.

We have now found that the reaction in toluene at room temperature between $P_2Ph_4$ and the 'solvent-stabilised intermediate[5]' $[Re_2Br_2(CO)_6(thf)_2]$ does not lead to P–P bond cleavage either. The title compound, giving analytical data in accord with the formula $Re_2Br_2(CO)_6P_2Ph_4$ was obtained as pale yellow crystals from toluene (reflux). It is diamagnetic [$\chi^{corr}$ = (Re) − 150 × $10^{-6}$ c.g.s. units at 22 °C] and shows four main i.r. carbonyl bands ($CCl_4$) at 2054, 2041, 1960, and 1923 cm$^{-1}$, very similar to those for the $S_2Ph_2$-complex.[3] The suggested similarity in structure was confirmed by a single-crystal *X*-ray analysis. *Crystal data:* $M$, 1070·7, triclinic, $a$ = 11·110(9), $b$ = 11·538(9), $c$ = 12·913(9) Å, $\alpha$ = 95·95(5), $\beta$ = 102·54(5), $\gamma$ = 95·92(5)°, $U$ = 1593·6 Å$^3$, $D_m$ = 2·23 g cm$^{-3}$, $Z$ = 2, $D_c$ = 2·23 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 108·2 cm$^{-1}$, space group $P\bar{1}$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the $\omega$–$2\theta$ scan technique. All reflections in one independent hemisphere out to $2\theta$ = 40° were measured; 2373 reflections were considered observed [$I \geqslant 3\sigma(I)$]. The structure was solved by Patterson and difference Fourier techniques, and refined to a conventional $R$ value of 0·072. The molecular arrangement around the rhenium atoms is shown in the Figure. Relevant structural parameters (average values) are: Re–Br, 2·649; Re–P, 2·510; Re–C, 1·81; P–P, 2·308 Å; ∠ Br–Re–Br, 82·6; Re–Br–Re, 94·6; Re–P–P, 108·2; P–Re–Br, 85·1°. The Re···Re distance is 3·891 Å [*cf.* 3·02 Å in the Re–Re bonded $Re_2(CO)_{10}$[6]], so we consider that metal–metal interaction is absent, in agreement with the $d^6$ configuration of the central metal atoms.

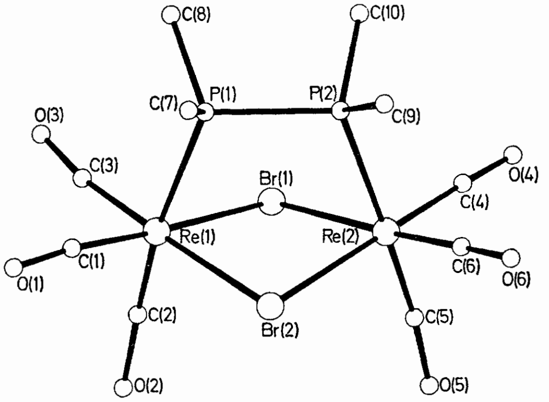
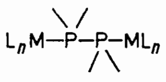


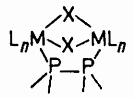
FIGURE. Molecular structure of $[Re_2Br_2(CO)_6P_2Ph_4]$ (only the *p*-bonded atom of each phenyl ring is shown, for clarity).

The P–P bonding distance of 2·308 Å compares reasonably well with the P–P distance of 2·277(4) Å found[7] for $[Ni_2(CO)_6P_2Ph_4]$, having a structural arrangement of type (**1**). The P–P distance in $P_2Me_4$ was found[8] to be 2·192 Å by an electron diffraction study.

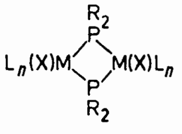
This molecule has some unique structural and chemical features. To the best of our knowledge, there is no precedent for a complex containing a $P_2R_4$ unit bridging two co-ordination polyhedra sharing a common edge, (**2**). The only known type of bridging arrangement for $P_2R_4$ is (**1**).[7,9] Moreover, chemical evidence exists that the molecular structure found for the $\mu$-tetraphenyldiphosphane–rhenium(I) complex is a stable one, since the system has no tendency to be converted thermally into the $\mu$-diphenylphosphido-derivative of rhenium(II) (**3**; M = Re, X = Br). We have verified that the reaction at reflux temperature (benzene) of $[ReBr(CO)_5]$ with $P_2Ph_4$ gives the same compound, as shown by analytical data, i.r. spectra, and *X*-ray powder patterns. The present results and comparison of the i.r. spectral data with those reported[10] for $[Re_2X_2(CO)_6$-$P_2Ph_4]$ (X = Cl or I) strongly suggest that the latter compounds, obtained by the reaction of $[ReX(CO)_5]$ with $P_2Ph_4$ in refluxing benzene and believed[10] to have a structure of type (**3**) should in fact be regarded as $\mu$-tetraphenyldiphosphane complexes of rhenium(I). The stability of the new molecular arrangement is also shown by the failure of the bromo-derivatives to react with thf even at reflux temperature, in contrast with the ready displacement of co-ordinated $S_2R_2$ by thf observed[3] for the $\mu$-$S_2R_2$ complexes.



(1)



(2)



(3)

The failure of $P_2Ph_4$ to be cleaved is surprising in view of the reported[11] weakness of the P–P bond and its reactivity with both nucleophilic and electrophilic reagents.[12]

We thank the U.S. National Science Foundation (University of Alabama and University of Houston) and the National Research Council, Rome (University of Pisa), for support, and the Scuola Normale Superiore, Pisa, for a foreign postdoctoral fellowship to I.P.M.

(*Received*, 1*st April* 1976; *Com.* 340.)

[1] L. F. Lindoy, *Co-ordination Chem. Rev.*, 1969, **4**, 41.

[2] J. Chatt and D. T. Thompson, *J. Chem. Soc.*, 1964, 2713.

[3] F. Calderazzo and D. Vitali, *Co-ordination Chem. Rev.*, 1975, **16**, 13.

[4] D. Vitali and F. Calderazzo, *Gazzetta*, 1972, **102**, 587.

[5] I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Gazzetta*; in the press.

[6] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

[7] R. H. B. Mais, P. G. Owston, D. T. Thompson, and A. M. Wood, *J. Chem. Soc.* (*A*), 1967, 744.

[8] A. McAdam, B. Beagley, and T. G. Hewitt, *Trans. Faraday Soc.*, 1970, **66**, 2732.

[9] J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 622; L. R. Nassimbeni, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 187; H. Hartung, *Z. anorg. Chem.*, 1970, **372**, 150.

[10] W. Hieber and W. Opavsky, *Chem. Ber.*, 1968, **101**, 2966.

[11] K. S. Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.

[12] R. F. Hudson, 'Organo-Phosphorous Chemistry,' Academic Press, New York, 1965.