TABLE I

PROPERTIES OF COMPOUNDS $N_3P_3(C_6H_5)_3(NHR)_3$

Compound	M.p., °C.	Mol. wt. Calcd.	Mol. wt. Found[a]	P–N freq., cm.$^{-1}$	P–C_6H_5 freq., cm.$^{-1}$	Analysis, %[b] C	H	N	P
$N_3P_3(C_6H_5)_3(NHn\text{-}C_3H_7)_3$						59.98	7.27	15.54	17.19
	92–93	540	519	1190, 1120	1440	60.15	7.19	15.34	17.20
	128–129	540	530	1190, 1128	1442	60.01	7.22	15.26	17.34
$N_3P_3(C_6H_5)_3(NHn\text{-}C_4H_9)_3$						61.83	7.78	14.42	15.95
	78–79	582	595	1185, 1123	1440	62.14	7.71	14.66	16.13
	97–98	582	595	1185, 1125	1440	61.47	7.78	14.35	15.85

[a] Ebullioscopic ($CHCl_3$ for propyl compound; C_6H_6 for butyl). [b] First line for each substance calculated; others found.

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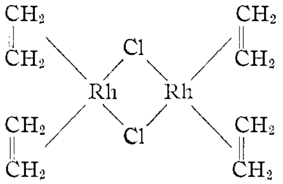
μ-Dichlorotetraethylenedirhodium(I)

Sir:

We wish to report the first synthesis of a coordination compound of monovalent rhodium and a monoölefin. μ-Dichlorotetraethylenedirhodium(I) is obtained with remarkable ease from



(I)

ethylene and hydrated rhodium(III) chloride in aqueous methanol. In this reaction (see eq. 1) rhodium(III) is reduced to rhodium(I), and an equivalent amount of ethylene is oxidized to acetaldehyde in a manner reminiscent of Smidt's[1] palladium-catalyzed aldehyde synthesis. The sparingly soluble orange-red complex (I) crystallizes from the reaction mixture. The stability of I is rather surprising in view of the lability of dichlorodiethyleneplatinum(II)[2] but may be ascribed to the high lattice energy of the solid as indicated by its low solubility.

$$2RhCl_3 + 2H_2O + 6C_2H_4 \longrightarrow \underset{(I)}{(C_2H_4)_4Rh_2Cl_2} + 2CH_3CHO + 4HCl \quad (1)$$

In a typical preparation, a solution of 20 g. of "rhodium trichloride trihydrate" (obtained from Engelhard Industries, actual composition $RhCl_{3.33}(H_2O)_{2.30}$) in 30 ml. of water was added to 500 ml. of methanol, and a slow stream of ethylene was bubbled through the stirred solution. After about 1 hr. the product began to crystallize, and, after 7 hr., 9.65 g. of I was collected by filtration, washed with methanol and ether, and dried in air. Further similar treatment of the filtrate with ethylene yielded 1.27 g. more of I. Since recrystallization of I is difficult, larger crystals suitable for X-ray diffraction measurements were obtained by a slower reaction at 0° with ethylene partial pressures of less than an atmosphere.

Elemental analyses correspond to the postulated composition. Calcd. for C_4H_8RhCl: C, 24.70; H, 4.15; Rh, 52.90; Cl, 18.23. Found C, 24.81; H, 4.17; Rh, 51.23; Cl, 18.26. Infrared absorption (KBr wafer) at 3.20 and 3.33 μ is attributed to the coördinated ethylene –C–H stretching vibration, while absorption at 6.58 μ is assigned to C=C stretching vibration.[3] Preliminary X-ray diffraction studies indicated that the crystals have a tetragonal structure and that the unit cell, which contains eight formula weights of the chlorine-bridged complex, has the dimensions A_0 = 10.07 Å., C_0 = 23.50 Å. Structures have been assigned to two related compounds on the basis of X-ray diffraction. Dahl, Martell, and Wampler[4] have reported that in red $(CO)_4Rh_2Cl_2$, the rhodium and bridging chloride ions lie in two planes which form an angle of 124°. Furthermore, $(CO)_4Rh_2Cl_2$ units appear to be connected by Rh–Rh bonds. On the other hand, Ibers and Snyder[5] ascribe a planar monomer structure to yellow $(C_8H_{14})Rh_2Cl_2$. On the basis of color and low solubility we are inclined to

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(1) J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1959).

(2) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

(3) (a) J. Chatt and L. A. Duncanson, *ibid.*, 2939 (1953); (b) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958); (c) H. B. Jonassen and J. E. Field, *J. Am. Chem. Soc.*, **79**, 1276 (1957).

(4) L. F. Dahl, C. Martell, and D. L. Wampler, *ibid.*, **83**, 1761 (1961).

(5) J. A. Ibers and R. G. Snyder, *ibid.*, **84**, 496 (1962).

expect that $(C_2H_4)_4Rh_2Cl_2$ will be found to be structurally similar to $(CO)_4Rh_2Cl_2$.

μ-Dichlorotetraethylenedirhodium is only sparingly soluble in such solvents as ethanol, acetone, dioxane, chloroform, or methylene chloride and generally cannot be recovered pure from these solvents. The solid is moderately stable. Samples occasionally darken after storage for several days at room temperature but are unaltered for months at 5°. Upon slow heating in an evacuated tube there is little change below 100°, but at 115° the surface of the crystals becomes black, and further heating causes rapid destruction without evidence of melting.

The coördinated ethylene of I is displaced by a number of ligands. For example, when suspensions in methanol were treated with cycloöctadiene, ethylene was displaced within 2 min., and the yellow μ-dichlorobis-(cycloöctadiene)-dirhodium(I) described by Chatt[6] precipitated. A similar displacement of ethylene occurred when I was treated with triphenylphosphine, hydrogen cyanide, acrylonitrile, or pyridine.

A propylene analog of I has been prepared from propylene and hydrated rhodium(III) chloride. It is more soluble and dissociates more readily than the ethylene complex in solution or when heated.

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[6] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

A Correction for the Lattice Constants of Mixed Metal Oxides of Rhenium and Osmium with the Hexagonal Barium Titanate Structure

Sir:

The correct lattice constants for the following compounds erroneously reported in *Inorganic Chemistry*, 1, 245 (1962) are

	a, Å.	*c*, Å.
$Ba_3Fe_2ReO_9$	5.81	14.10
$Ba_3Cr_2ReO_9$	5.70	13.8
Ba_2MnOsO_6	5.82	14.2
Ba_2FeOsO_6	5.76	14.1

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Book Review

A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis. Third Enlarged Edition. By ARTHUR I. VOGEL, Woolwich Polytechnic, London. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. (and Longmans, Green and Co., Ltd.), 1961. xxx + 1216 pp. 16 × 23 cm. Price, $12.00.

Here, indeed, is a book! The comprehensive versatility of this author, whose texts on practical organic chemistry and qualitative analysis are equally well known, is admirably demonstrated in this expanded version of his work on quantitative inorganic analysis. One cannot resist the temptation to compare this work with another having similar aims and scope (though, only 700 pp.), namely, Charlot and Bezier's "Quantitative Inorganic Analysis." It is the latter work which tends to suffer by the comparison. The less critical choice of some procedures and their abbreviated descriptions, and the superficiality with which the theory and practice of some techniques are outlined, comprise possible objections to any such ambitious a coverage in a one-volume treatise. Though using 1246 pages in the process, Dr. Vogel has, by and large, succeeded in avoiding both criticisms.

Represented as being a student text suitable for his entire training in this area and as being of value to practicing analytical chemists, this book is fairly described as being *all* of that. The theory and practice of classical gravimetric and titrimetric methods are adequately treated. Advantageous and proven newer reagents and techniques applicable to "wet chemical" procedures are described for *use*, and not merely added as a weak appendage indiscriminately enumerating *all* that is new. A similar comment applies with respect to the inclusion of good methods for such elements as molybdenum, zirconium, uranium, etc. An excellent chapter on complexometric titrations is largely devoted to the applications of ethylenediaminetetraacetic acid (EDTA).

The practical and theoretical coverage of "instrumental" measuring techniques is very good and embraces most of the more familiar and consequential electrical and optical themes. Certain specialized techniques (such as the use of X-rays, Raman spectroscopy, radiochemical methods, nuclear magnetic resonance spectroscopy, etc.) are, understandably, not treated. Details on separations *via* distillation and gas (adsorption) chromatography are not given, on the grounds that these are of more general value in organic work. Gas-evolution techniques are concisely treated, however, and a detailed chap-