

of the active nitrogen with NO_2 ,² it was found that the atomic nitrogen concentration over the carbon was the same whether pure nitrogen or the nitrogen-hydrogen mixture was used. Assuming the hydrogen was completely dissociated over the carbon, it was found that the N:H ratio over the carbon was at least 10:1. It is hypothesized that the atomic nitrogen is chemisorbed on the carbon and that this chemisorbed nitrogen perturbs the adjacent carbon-carbon bonds. A hydrogen atom then reacts with the chemisorbed CN forming HCN with a collision efficiency of at least 10^{-3} . It is known that at 600° hydrogen atoms react in an analogous way with cyanogen.³

This research was carried out at the General Electric Company Missile and Space Vehicle Department, Aerosciences Laboratories, Philadelphia, Pa., under sponsorship of the Ballistic Missile Division, U. S. Air Force, Contract No. 04(647)-269, and a detailed account of it is to be published elsewhere.⁴

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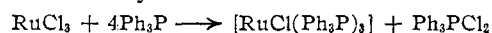
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RECEIVED JANUARY 11, 1960

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Sir:

We wish to report a new type of ruthenium complex, in which the central atom displays the unusual oxidation state I. Chloro-tris-(triphenylphosphine)-ruthenium(I) is obtained in 96% yield by treating ruthenium(III) chloride¹ with an excess of triphenylphosphine (P/Ru, 6-12/1) in boiling ethylene glycol monomethyl ether (124°), the tertiary phosphine being the sole reducing agent in the system



Anal. Calcd. for $\text{RuClP}_3\text{C}_{54}\text{H}_{45}$: Ru, 10.95; Cl, 3.84; P, 10.06; C, 70.24; H, 4.91. Found: Ru, 11.27; Cl, 3.80; P, 9.85; C, 69.09; H, 4.89.

The yellow crystals of the univalent complex are stable in air (m.p. 139°) and essentially diamagnetic ($\mu_{\text{eff}} = 0.28$ B.M., 27°). The compound is a non-electrolyte in nitrobenzene ($\Lambda_M = 0.2$ for a 6×10^{-4} molar solution); its apparent molecular weight in chloroform, 492, indicates extensive dissociation (formula weight, 923), and is therefore inconclusive with respect to the possible presence of a polynuclear species.

The corresponding triphenylarsine derivative, $\text{RuCl}(\text{Ph}_3\text{As})_3$, is synthesized in an analogous manner, but the compound results only after prolonged refluxing. (*Anal.* Calcd. for $\text{RuClAs}_3\text{C}_{54}\text{H}_{45}$: Ru,

(1) Commercial "hydrated ruthenium chloride"; analysis in this laboratory gave Ru/Cl = 1/2.84.

9.58; Cl, 3.36; As, 21.30; C, 61.46; H, 4.30. Found: Ru, 9.36; Cl, 3.69; As, 20.65; C, 61.03; H, 4.52.) Even more vigorous conditions are required for the preparation of bromo-tris-(triphenylphosphine)-ruthenium(I): the complex is formed from RuBr_3 and $(\text{C}_6\text{H}_5)_3\text{P}$ in ethylene glycol at 190° . (*Anal.* Calcd. for $\text{RuBrP}_3\text{C}_{54}\text{H}_{45}$: Ru, 10.45; Br, 8.26; P, 9.60; C, 67.01; H, 4.69. Found: Ru, 10.98; Br, 8.29; P, 9.38; C, 66.78; H, 4.99.)

According to their X-ray powder diffraction patterns the Ru(I) complexes with triphenylphosphine and triphenylarsine are isomorphous with each other, and with the recently discovered osmium complexes of the same type, $[\text{OsX}(\text{Ph}_3\text{M})_3]$ (X = Cl, Br; M = P, As).² The chemical properties of the univalent osmium and ruthenium complexes are also rather similar. Generally, the ruthenium(I) compounds appear to be more reactive with respect to dissociation.

The diamagnetism of $[\text{RuCl}(\text{Ph}_3\text{P})_3]$ suggests exchange interaction between two neighboring ruthenium(I) atoms of d^7 configuration, and thus a dimeric structure which would provide for a relatively short Ru-Ru distance (*cf.* ref. 2). Regardless of what the actual configuration of the complex may be, it seems likely that ruthenium is effectively quinequivalent. This is reminiscent of the quinequivalent iron(I) complex, $[\text{Fe}(\text{CO})_2(\text{diarsine})\text{I}]$, reported recently by Nigam, Nyholm and Rao,³ who also point out that there exists a whole series of isoelectronic (d^7) quinequivalent compounds: Mn(O), Fe(I), Co(II), and Ni(III) (for references, see 3). These complexes are monomeric and *paramagnetic*, however, and therefore not strictly analogous with the present case.

The only solid compound presumed to contain Ru(I), $\text{RuX}(\text{CO})$ (X = Br, I),^{4,5} that has been reported previously, is most likely a polymer of unknown complexity.⁵ Jørgensen⁶ summarizes critically the many arguments concerning the existence of ruthenium(I) in aqueous solution (for references, see ref. 6), and concludes that Ru(I) disproportionates in a few minutes to the metal and Ru(II).

Other new complexes of ruthenium with triphenylphosphine and triphenylarsine which have been synthesized in the present study include $(\text{Ru}^{\text{II}}\text{Cl}_2(\text{Ph}_3\text{P})_3)_n$, $[\text{Ru}^{\text{III}}\text{Cl}_3(\text{Ph}_3\text{As})_3]$ and $[\text{Ru}^{\text{III}}\text{X}_3(\text{Ph}_3\text{M})_2]$ (X = Cl, Br; M = P, As). Details of this and related work will be reported in a later communication.

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RECEIVED JANUARY 13, 1960

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