differences in kinetic behavior (*i.e.*, steady state *vs.* pre-equilibrium) between this reaction and those described earlier.

Tetrakis(triphenylphosphine)platinum(0) and Tris(tri-phenylphosphine)platinum(0). The addition of excess triphenylphosphine to a benzene solution of PtL_2-(C_2H_4) results in quantitative displacement of the ethylene from the complex. The absorbance of a 2.4×10^{-3} M $PtL_2(C_2H_4)$ solution (which had previously been purged with nitrogen to lower the ethylene concentration), throughout the wavelength range 400–560 mμ, was found initially to increase linearly with the amount of added L and to attain a limiting value when the ratio of added L to initial $PtL_2(C_2H_4)$ exceeded 1:1. The displacement of ethylene thus appears to conform quantitatively to

$$PtL_2(C_2H_4) + L \rightleftharpoons PtL_3 + C_2H_4 \qquad (10)$$
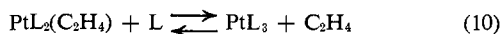
The final spectrum of the solution (invariant to the addition of up to 2.4×10^{-2} M excess L) was found to be identical with that of a solution of PtL_4 of the same platinum concentration. It is concluded that the predominant species present in both solutions is the tris complex, PtL_3, and that both dissociation (*i.e.*, to PtL_2) and association (*i.e.* to PtL_4) are negligible over a wide range of L concentration.[7,7a] The constant spectrum which we ascribe to PtL_3 exhibits the following extinction coefficients (in parentheses) at the indicated wavelengths: 520 mμ (25 M^{-1} cm^{-1}), 500 (70), 480 (2 $\times$ 10^2), 460 (4 $\times$ 10^2), 440 (6 $\times$ 10^2), 420 (1.2 $\times$ 10^3).

In further support of the above conclusion, we found that identical rates of reaction with oxygen (determined spectrophotometrically by following the disappearance of PtL_3) were exhibited by solutions prepared by both of the above procedures, *i.e.*, (i) by dissolving PtL_4 in benzene or (ii) by adding 1 mole of L per mole of $PtL_2(C_2H_4)$ to a solution of the latter. The reaction with O_2, which yields the known[3,8] complex PtL_2O_2, in accord with

$$PtL_3 + O_2 \longrightarrow PtL_2O_2 + L \qquad (11)$$
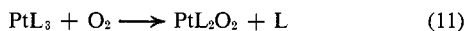
exhibited the rate law, $-d[PtL_3]/dt = k_3[PtL_3][O_2]$, where $k_3 = 2.6 \pm 0.1$ M^{-1} sec^{-1}. The rate of this reaction was unaffected by addition of up to 3×10^{-3} M excess L but, in accord with earlier reports,[8] we also found that PtL_2O_2 does react further with excess L to regenerate PtL_3, *i.e.*

$$PtL_2O_2 + 3L \longrightarrow PtL_3 + 2LO \qquad (12)$$
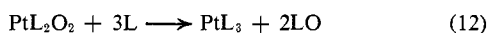
so that a catalytic cycle for the oxidation of triphenylphosphine to triphenylphosphine oxide is established. Reaction 12 exhibited the rate law, $d[PtL_3]/dt = k_4 \cdot [PtL_2O_2][L]$ where $k_4 = 0.15 \pm 0.01$ M^{-1} sec^{-1}. A possible mechanism for the latter reaction (which may

(7) This conclusion is at variance with an earlier report[1] that PtL_4 (mol wt 1244) in benzene exhibits an apparent cryoscopic molecular weight of 400, suggesting dissociation according to $PtL_4 \rightarrow PtL_2 + 2L$. The molecular weight determination is complicated by the extreme sensitivity of the compound to oxygen, and it is possible that the discrepancy cited results from a lowering of the apparent molecular weight by the reaction, $PtL_4 + O_2 \rightarrow PtL_2O_2 + 2L$.

(7a) NOTE ADDED IN PROOF. From the inverse dependence of the rate of the reaction, $PtL_2 + Ph_3SnCl \rightarrow PtL_2(SnPh_3)Cl$, on the concentration of L, we have now been able to estimate the equilibrium constant of the dissociation reaction, $PtL_3 \rightleftharpoons PtL_2 + L$, in benzene solution, to be 1×10^{-4} M.

(8) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, **79**, 62 (1967).

also have relevance to the reactions[9] of PtL_2O_2 with SO_2 and NO_2), involving a dissociative "oxygen insertion" step, is suggested below.
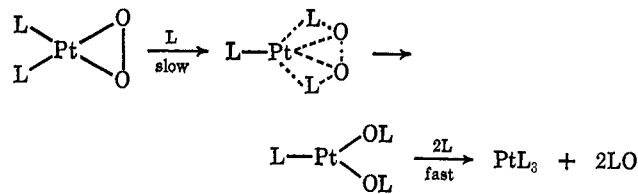
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Electrolytic Reduction of Molecular Nitrogen

Sir:

Inorganic chemical endeavors in this laboratory during the past several years have been concerned with the fixation–reduction of molecular nitrogen[1] promoted under mild conditions in solution by lower valent titanium species.[2] By such means, formation of ammonia involving hydrogen abstraction from solvent has been observed;[1] a cyclic, over-all catalytic ammonia synthesis involving a protonation operation has been developed;[3] and the copious, single-stage reduction of *aerial* nitrogen to ammonia has been discovered.[3,4] In all these processes, alkali metal or naphthalene radical anion (naphthalide) served in the capacity of reducing agent. As the find in a search for alternate, more practical electron sources, we have now achieved significant *electrolytic* reduction of molecular nitrogen to the ammonia level, also a room-temperature and atmospheric-pressure procedure utilizing a titanium-coordinating species.

The electrolysis medium consisted of a solution of titanium tetraisopropoxide and aluminum chloride (molar ratio 1:1.5) in 1,2-dimethoxyethane. During the electrolysis nitrogen gas was bubbled through the electrolysis cell, usually a single-compartment type equipped with platinum electrodes. In a typical experiment, a solution of 10 mmol of titanium isopropoxide and 15 mmol of aluminum chloride in 20 ml of dry solvent was subjected for 2 days to a 90-V electrolysis, initially at 50 mA. From time to time, the polarity was reversed. After hydrolysis, the product ammonia was detected qualitatively by the Berthelot test and quantitatively by titration (*ca.* 10% yield, based on NH_3:Ti molar ratio). When argon was used in place of nitrogen, no ammonia could be detected. When the titanate ester was omitted, no ammonia was formed, an

(1) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Am. Chem. Soc.*, **89**, 5707 (1967). For results from other laboratories, see references cited in this publication.

(2) See E. E. van Tamelen and M. A. Schwartz, *ibid.*, **87**, 3277 (1965), for initial work based on the titanium(II) concept.

(3) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968).

(4) *Cf.* A. D. Allen and F. Bottomley, *Can. J. Chem.*, **46**, 469 (1968).

observation in keeping with the idea that the aluminum chloride functions mainly as an electrolyte. However, whereas a solution of aluminum chloride can be electrolyzed for several days without amperage decrease, the current rapidly drops and reaches zero in about 2 days when the titanate ester–aluminum chloride combination is used.[5]

Titanium must be reduced beyond the III state before appreciable amounts of nitrogen are reduced, as shown by a rough calculation of the amount of current having passed through the cell at the point where ammonia could first be detected. Also, in an experiment conducted in a divided cell, the solution in the cathode compartment rapidly turned blue during the electrolysis, suggesting the presence of Ti(III) in the solution. When approximately 1 mol equiv of electrons/mole of titanium had been passed through the cell, the solution started to turn black (indicating further reduction of titanium) and thereupon ammonia began to appear in bound form. When titanium trichloride was used in place of titanium tetraisopropoxide, ammonia was detected after hydrolysis at a point in time when considerably less (ca. 10%) electrons per mole of titanium had passed through the solution. The significance of this experiment is not clear, however, since only 1.5% ammonia was formed.

Despite the modest yields of ammonia but because of the practical import, the above preliminary findings are being communicated at this early stage. The nature of the titanium agent in this and related fixation–reduction experiments[1,3] is under active investigation and will, it is hoped, constitute the subject of a future publication.

(5) Since the bound nitrogen in complexes like $Os=N^+=N^-$ probably has basic character, the aluminum chloride might be tied up in part as an acceptor of the N_2 ligand in a titanium coordination compound.

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Synthesis and Structure of the Six-Coordinate Hexaisothiocyanatolanthanide(III) Complexes[1]

Sir:

Although there has been an increased interest in the coordination chemistry of the lanthanide ions during the past decade, most of this work has been concerned with complexes in which the coordination number of the lanthanide ion is greater than six.[2] It has become increasingly apparent that there are very few six-coordi-

(1) This work was supported by grants from the National Science Foundation and the Petroleum Research Fund as well as by the Graduate Divisions of the University of Minnesota and Wayne State University. We also gratefully acknowledge the contribution of the Wayne State University Computing Center.

(2) For recent reviews, see T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrús, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965); T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gayhart, "Progress in the Science and Technology of the Rare Earths," Vol. III, L. Eyring, Ed., Pergamon Press, Oxford, England, in press.

nate complexes of the trivalent lanthanide ions and that one must show extreme caution in formulating six-coordination. We wish to report the preparation and some properties of the tetra-*n*-butylammonium salts of the hexaisothiocyanato complexes of the trivalent lanthanides[3] and, moreover, the results of an X-ray structure determination of the erbium compound. To the best of our knowledge, this is the first structure determination on a discrete six-coordinate lanthanide complex.

The complexes of the heavier lanthanides are deposited in crystalline form from ethanol solutions containing the appropriate hydrated lanthanide chloride and tetra-*n*-butylammonium thiocyanate in the molar ratio of 1:10. The complexes of the lighter lanthanides crystallize slowly from a 1:1 ethyl alcohol–*t*-butyl alcohol solution of the lanthanide thiocyanate and tetra-*n*-butylammonium thiocyanate in a 1:3 molar ratio. The total analysis of the yttrium complex was as follows. *Anal.* Calcd for $\{(C_4H_9)_4N\}_3Y(NCS)_6$: C, 55.7; H, 9.4; S, 16.5; N, 10.8; Y, 7.7; SCN⁻, 29.9. Found: C, 55.6; H, 9.3; S, 15.8; N, 10.8; Y, 7.7; SCN⁻, 29.7. In addition satisfactory analyses for Ln^{3+} and SCN⁻ have been obtained for the praseodymium, neodymium, europium, samarium, holmium, erbium, thulium, and ytterbium compounds.

The complexes melt without apparent decomposition at temperatures less than 200° and are soluble in a number of organic solvents such as dichloromethane, nitromethane, nitrobenzene, acetonitrile, methanol, and ethanol. They are soluble in water upon heating and are subsequently decomposed. The molar conductances of solutions of three of the complexes in nitromethane and nitrobenzene are within the range expected for 3:1 electrolytes.[4] The conductances of the complexes of the lighter lanthanides are at the upper end of this range, probably indicating that additional dissociation is occurring. This is supported by the spectral measurements in the visible region.

The infrared spectra are suggestive of N-coordination[5] but are not conclusive since there is little shift in the bands due to the thiocyanate groups, an observation which is consistent with the weak polarizing properties of the lanthanide ions. The main absorption bands in KBr or Nujol are given below for a typical complex.

	ν_{CN}	ν_{NCS}
$(C_4H_9)_4NCNS$	2060	465, 480
$\{(C_4H_9)_4N\}_3Er(NCS)_6$	2090 sh, 2045	480

The colors of the compounds are characteristic of the particular lanthanide ion but are very pale. (It should be noted that those ions which should give colorless compounds yield complexes which are very faintly orange due to the presence of *ca.* 0.01% iron.) The absorption spectra have been measured on dichloromethane solutions and the diffuse reflectance spectra have been measured for powdered samples. The reflectance spec-

(3) A. M. Golub, M. I. Olevinskii, and N. S. Zhiguline (*Zh. Neorgan. Khim.*, **11**, 1574 (1966)) have previously reported $(NH_4)_3Nd(NCS)_6 \cdot 4C_2H_5OH$ and $Na_3La(NCS)_6 \cdot 3C_2H_5OH$.

(4) The molar conductances of the complexes of Y, Er, and Nd were measured in nitromethane to be 241, 237, 284 ohm⁻¹, respectively; expected range for 3:1 electrolyte, 230–280 ohm⁻¹: N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959). The molar conductances of these complexes in nitrobenzene are 59, 62, 73 ohm⁻¹; expected range for 3:1 electrolyte (extrapolated), 60–90 ohm⁻¹: D. J. Phillips and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).

(5) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).