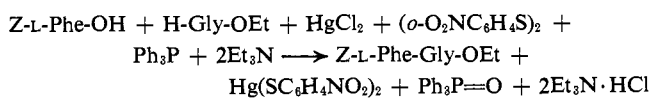


derivative, $[\alpha]^{20D} - 16.7^\circ$ (*c* 2, EtOH), was obtained by chromatography on silica gel, giving total yield 96%.

In this new method the NPS group, which has been known as a protecting group of the amino function, can actually be used as a reactive site to afford amide. It should be noted that this fact gives the NPS group a novel meaning of an activatable protecting group in peptide synthesis.

This method was further extended to the synthesis of peptide starting from the free N-protected amino acid and free amino acid ester. When equimolar amounts of benzyloxycarbonyl-L-phenylalanine, mercury(II) chloride, ethyl glycinate, di-*o*-nitrophenyl disulfide, and triphenylphosphine in methylene chloride were mixed at room temperature for 3 hr, benzyloxycarbonyl-L-phenylalanyl-glycine ethyl ester was obtained in 89% yield, mp 110–110.5°, $[\alpha]^{20D} - 17.1^\circ$ (*c* 2, EtOH).



Of various metal salts examined, those of the so-called soft metals proved to be very effective for this type of reaction.

Teruaki Mukaiyama, Masaaki Ueki
Hiroshi Maruyama, Rei Matsueda

Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan

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Substitution and Oxidative Addition Reactions of Platinum(0) Complexes. Evidence for Coordinatively Unsaturated Species in Solution and as Reactive Intermediates

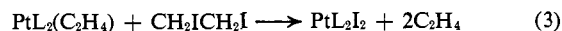
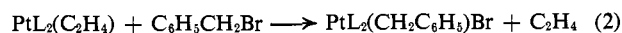
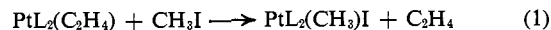
Sir:

Since the discovery¹ in 1958 of the zerovalent platinum compounds, PtL_4 and PtL_3 ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$), the study of these and other zerovalent platinum compounds, such as $\text{PtL}_2(\text{C}_2\text{H}_4)$,² and of their substitution and oxidative addition reactions has attracted great interest.^{3–5} The investigations reported thus far, however, have not served to establish conclusively either the nature of the species present in solutions of PtL_4 and related compounds or the mechanisms of their reactions.

We report here preliminary results of several investigations which have a bearing on these important questions and, in particular, which serve to establish (i) that PtL_4 and $\text{PtL}_2(\text{C}_2\text{H}_4)$ are extensively dissociated in benzene solution to PtL_3 and PtL_2 , respectively, and (ii) that the latter, coordinatively unsaturated, species are the reactive intermediates in certain substitution and oxidative addition reactions of the parent compounds.

Bis(triphenylphosphine)(ethylene)platinum(0). The kinetics of the following reactions of $\text{PtL}_2(\text{C}_2\text{H}_4)$ were examined at 25° in benzene solution over a wide range of initial concentrations of the reactants (*ca.* 4×10^{-4} to 1×10^{-3} *M* $\text{PtL}_2(\text{C}_2\text{H}_4)$, 0.1–1 *M* organic halide) and of added ethylene (3×10^{-4} to 1.5×10^{-1} *M*).

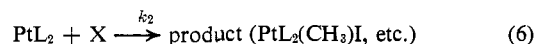
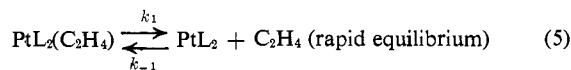
- (1) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).
- (2) C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, 3, 31 (1967); *J. Am. Chem. Soc.*, 90, 1464 (1968).
- (3) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, 45, 301 (1967).
- (4) L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).
- (5) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 5, 1128 (1966).



In each case the kinetics, measured spectrophotometrically, conformed to the rate law

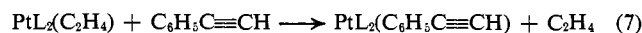
$$-d \ln [\text{PtL}_2(\text{C}_2\text{H}_4)]_{\text{tot}}/dt = k_{\text{obsd}} = k_2 K [\text{X}] / (K + [\text{C}_2\text{H}_4]) \quad (4)$$

consistent with the following mechanism



where $\text{X} = \text{CH}_3\text{I}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, or $\text{CH}_2\text{I}(\text{CH}_2)\text{I}$, $[\text{PtL}_2(\text{C}_2\text{H}_4)]_{\text{tot}} = [\text{PtL}_2(\text{C}_2\text{H}_4)] + [\text{PtL}_2]$, and $K = (k_1/k_{-1})$, *i.e.*, the equilibrium constant for the dissociation of $\text{PtL}_2(\text{C}_2\text{H}_4)$ according to eq 5. In accord with eq 4, the kinetic data yielded linear plots of $k_{\text{obsd}}^{-1}[\text{X}]$ vs. $[\text{C}_2\text{H}_4]$ from the slopes of which the values of $k_2 K$, 3.8×10^{-5} , 4.2×10^{-4} , and 7.5×10^{-3} sec^{-1} , were obtained for CH_3I , $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, and $\text{CH}_2\text{I}(\text{CH}_2)\text{I}$, respectively. The small intercepts of these plots precluded accurate determination of the separate values of k_2 and K ; however, to within the accuracy indicated, all the data could be accommodated by the value $K = (3.0 \pm 1.5) \times 10^{-3}$ *M*, yielding the corresponding values of 1.3×10^{-2} , 1.4×10^{-1} , and 2.5 $\text{M}^{-1} \text{sec}^{-1}$, respectively, for k_2 . The above value of K implies considerable dissociation of $\text{PtL}_2(\text{C}_2\text{H}_4)$ over the range of ethylene concentrations examined, ranging from about 2% at 0.15 *M* C_2H_4 to 90% at 3×10^{-3} *M* C_2H_4 .

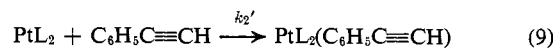
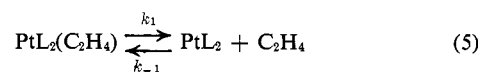
Some kinetic measurements were also made on the substitution reaction



Two distinct reactions were observed. An initial, immeasurably fast, reaction is attributed to the combination of $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ with the PtL_2 initially present in equilibrium with $\text{PtL}_2(\text{C}_2\text{H}_4)$. A subsequent slower reaction obeyed the rate law

$$-d \ln [\text{PtL}_2(\text{C}_2\text{H}_4)]/dt = k_1 k_2' [\text{C}_6\text{H}_5\text{C}\equiv\text{CH}] / (k_{-1} [\text{C}_2\text{H}_4] + k_2' [\text{C}_6\text{H}_5\text{C}\equiv\text{CH}]) \quad (8)$$

derived for the mechanism

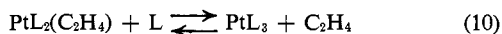


This is analogous to the mechanism of acetylene replacement in complexes of the type $\text{PtL}_2(\text{acetylene})$, previously found by Allen and Cook.⁶ Kinetic measurements over the concentration ranges, 3×10^{-4} to 0.15 *M* C_2H_4 and 8×10^{-4} to 6×10^{-2} *M* $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$, yielded the values, $k_1 = 0.33$ sec^{-1} and $k_{-1}/k_2' = 0.39$. Using the previously determined value of $K (=k_1/k_{-1}) = 3 \times 10^{-3}$ *M* yields $k_{-1} = 1.1 \times 10^2$ and $k_2' = 2.8 \times 10^2$ $\text{M}^{-1} \text{sec}^{-1}$. The much higher reactivity of $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ (compared with that of CH_3I , $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, or $\text{CH}_2\text{I}(\text{CH}_2)\text{I}$) toward PtL_2 accounts for the

- (6) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 41, 1235 (1963); 42, 1963 (1964).

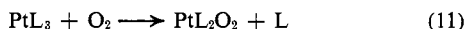
differences in kinetic behavior (*i.e.*, steady state *vs.* pre-equilibrium) between this reaction and those described earlier.

Tetrakis(triphenylphosphine)platinum(0) and Tris(triphenylphosphine)platinum(0). The addition of excess triphenylphosphine to a benzene solution of $\text{PtL}_2(\text{C}_2\text{H}_4)$ results in quantitative displacement of the ethylene from the complex. The absorbance of a $2.4 \times 10^{-3} M$ $\text{PtL}_2(\text{C}_2\text{H}_4)$ solution (which had previously been purged with nitrogen to lower the ethylene concentration), throughout the wavelength range 400–560 $m\mu$, 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 $\text{PtL}_2(\text{C}_2\text{H}_4)$ exceeded 1:1. The displacement of ethylene thus appears to conform quantitatively to

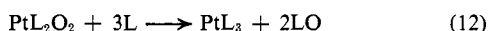


The final spectrum of the solution (invariant to the addition of up to $2.4 \times 10^{-2} M$ excess L) was found to be identical with that of a solution of PtL_4 of the same platinum concentration. It is concluded that the predominant species present in both solutions is the tris complex, PtL_3 , and 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 $m\mu$ ($25 M^{-1} \text{cm}^{-1}$), 500 (70), 480 (2×10^2), 460 (4×10^2), 440 (6×10^2), 420 (1.2×10^3).

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 $\text{PtL}_2(\text{C}_2\text{H}_4)$ to a solution of the latter. The reaction with O_2 , which yields the known^{3,8} complex PtL_2O_2 , in accord with



exhibited the rate law, $-d[\text{PtL}_3]/dt = k_3[\text{PtL}_3][\text{O}_2]$, where $k_3 = 2.6 \pm 0.1 M^{-1} \text{sec}^{-1}$. The rate of this reaction was unaffected by addition of up to $3 \times 10^{-3} M$ 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.*



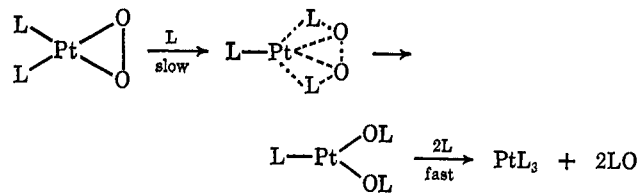
so that a catalytic cycle for the oxidation of triphenylphosphine to triphenylphosphine oxide is established. Reaction 12 exhibited the rate law, $d[\text{PtL}_3]/dt = k_4[\text{PtL}_2\text{O}_2][\text{L}]$ where $k_4 = 0.15 \pm 0.01 M^{-1} \text{sec}^{-1}$. A possible mechanism for the latter reaction (which may

(7) This conclusion is at variance with an earlier report¹ that PtL_4 (mol wt 1244) in benzene exhibits an apparent cryoscopic molecular weight of 400, suggesting dissociation according to $\text{PtL}_4 \rightarrow \text{PtL}_2 + 2\text{L}$. 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, $\text{PtL}_4 + \text{O}_2 \rightarrow \text{PtL}_2\text{O}_2 + 2\text{L}$.

(7a) NOTE ADDED IN PROOF. From the inverse dependence of the rate of the reaction, $\text{PtL}_2 + \text{Ph}_3\text{SnCl} \rightarrow \text{PtL}_2(\text{SnPh}_3)\text{Cl}$, on the concentration of L, we have now been able to estimate the equilibrium constant of the dissociation reaction, $\text{PtL}_3 \rightleftharpoons \text{PtL}_2 + \text{L}$, in benzene solution, to be $1 \times 10^{-4} M$.

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

also have relevance to the reactions⁹ of PtL_2O_2 with SO_2 and NO_2), involving a dissociative "oxygen insertion" step, is suggested below.



Acknowledgments. Support through grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(9) C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **89**, 3066 (1967).

J. P. Birk, Jack Halpern, A. L. Pickard

Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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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 nitrogen¹ 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 $\text{NH}_3:\text{Ti}$ 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).