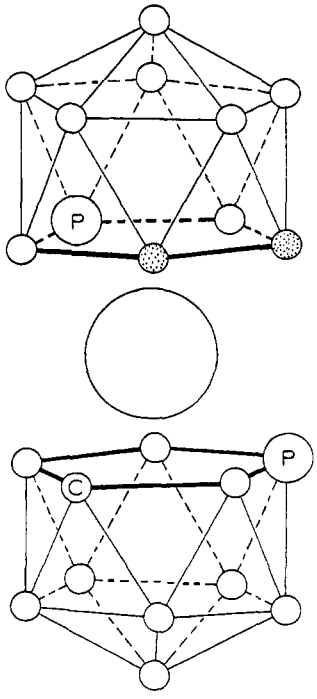

Figure 1. An idealized view of the molecular structure; the exocyclic methyl groups are not shown. The established position for the carbon atom in one of the complexing rings is marked. The partial carbon sites in the other ring are dotted. The perpendicular distance of the iron atom from the ring is 1.47 Å; the average P–C, P–B, B–B, and B–C distances are 1.80, 1.90, 1.81, and 1.71 Å, respectively.

and Co(II). The neutral mixed ligand compounds, π-$C_5H_5Fe[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]$ and $[(3)\text{-}1,7\text{-}B_9H_9CHPCH_3]Mn(CO)_3$ have been obtained by procedures similar to those described previously.[4] Analyses of representative compounds are given in Table I. A large family of these compounds probably exists, and an extensive study of this area is in progress.

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A New Method for Peptide Synthesis by Oxidation–Reduction Condensation

Sir:

This communication reports a new and useful method for the synthesis of peptides by the use of sulfenamide as an amino component. It is known that the sulfenamide group obtained from sulfenyl chloride and amines can be employed as a useful protecting group in peptide synthesis.[1,2] The sulfenyl group can be readily removed by treatment with mercaptan.[3] The enhanced reactivity of mercaptan toward sulfenamide is believed to be owing to the "soft" nucleophilicity of mercaptan and, of equal importance, to the ability to protonate the nitrogen atom of the sulfenamide. The latter was ascertained by the following experiments. A rapid reaction took place to yield amine, mercaptan or sulfide, and phosphine oxide when sulfenamide was treated with another "soft" nucleophile, triphenylphosphine, in the presence of either water or alcohol. On the contrary, no detectable change was observed when the reaction was carried out in the absence of these active hydrogen compounds. On this basis, it was found that carboxamide was formed when carboxylic acid was used in the above-mentioned reaction. Unfortunately, this reaction is not sufficiently quantitative for the preparative method of carboxamide because of the undesirable side reaction of mercaptan produced with sulfenamide. This difficulty was overcome by the use of carboxylic acid as its copper(II) salt, by which the mercaptide anion is captured as copper mercaptide.

$$(R^1CO_2)_2Cu + 2R^2SNR^3R^4 + 2Ph_3P \longrightarrow 2R^1CONR^3R^4 + [(R^2S)_2Cu] + 2Ph_3P{=}O$$

In a typical experiment, N-*n*-butylbenzenesulfenamide (10 mmol) in methylene chloride was added at room temperature to a stirred mixture of copper(II) *n*-capronate (5 mmol) and triphenylphosphine (10 mmol) in methylene chloride. After stirring for an additional 3 hr, the precipitated copper mercaptide was filtered off and the solvent was evaporated *in vacuo*. From the residue triphenylphosphine oxide resulted as crystals, mp 154–156°, 2.60 g (93%), and N-*n*-butyl-*n*-capronamide was obtained by distillation as a colorless liquid, bp 95–98° (0.05 mm), 1.63 g (95%).

On the other hand, when N-benzyl-*o*-nitrobenzenesulfenamide (10 mmol) was allowed to react with copper(II) benzoate (5 mmol) and triphenylphosphine (10 mmol) in methylene chloride at room temperature, N-benzylbenzamide could not be detected in tlc. However, the reaction began to take place rapidly by the further addition of 10 mmol of the phosphine to the reaction mixture, resulting in the formation of N-benzylbenzamide in 90% yield along with about 15 mmol of triphenylphosphine oxide.

Next, this method was applied to peptide synthesis by treating copper(II) benzyloxycarbonyl-L-phenylalaninate (5 mmol) and N-(*o*-nitrophenylsulfenyl)glycine ethyl ester (10 mmol) with triphenylphosphine (20 mmol) in methylene chloride at room temperature. The reaction took place soon after the addition of phosphine; NPS-glycine ester disappeared within 3 hr and only three spots of metallic compound, dipeptide derivative, and phosphine oxide were detected on tlc. After removal of the solvent the residue was dissolved in methanol–ether. Then the addition of petroleum ether gave 2.60 g (68%) of benzyloxycarbonyl-L-phenylalanylglycine ethyl ester, which was recrystallized from ethyl acetate–petroleum ether, mp 109–112°, $[\alpha]^{20}D$ −17.0° (*c* 2, EtOH) [lit.[4] mp 110–113°, $[\alpha]^{25}D$ −16.6° (*c* 2, EtOH)]. An additional 1.10 g of dipeptide

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derivative, $[\alpha]^{20}D$ −16.7° (*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-phenylalanylglycine ethyl ester was obtained in 89% yield, mp 110–110.5°, $[\alpha]^{20}D$ −17.1° (*c* 2, EtOH).

$$\text{Z-L-Phe-OH} + \text{H-Gly-OEt} + HgCl_2 + (o\text{-}O_2NC_6H_4S)_2 + Ph_3P + 2Et_3N \longrightarrow \text{Z-L-Phe-Gly-OEt} + Hg(SC_6H_4NO_2)_2 + Ph_3P{=}O + 2Et_3N\cdot HCl$$

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

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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 discovery[1] in 1958 of the zerovalent platinum compounds, PtL_4 and PtL_3 (L = $P(C_6H_5)_3$), the study of these and other zerovalent platinum compounds, such as $PtL_2(C_2H_4)$,[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 $PtL_2(C_2H_4)$ 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 $PtL_2(C_2H_4)$ 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* $PtL_2(C_2H_4)$, 0.1–1 *M* organic halide) and of added ethylene (3×10^{-4} to 1.5×10^{-1} *M*).

$$PtL_2(C_2H_4) + CH_3I \longrightarrow PtL_2(CH_3)I + C_2H_4 \quad (1)$$

$$PtL_2(C_2H_4) + C_6H_5CH_2Br \longrightarrow PtL_2(CH_2C_6H_5)Br + C_2H_4 \quad (2)$$

$$PtL_2(C_2H_4) + CH_2ICH_2I \longrightarrow PtL_2I_2 + 2C_2H_4 \quad (3)$$

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

$$-\mathrm{d}\ln[PtL_2(C_2H_4)]_{tot}/\mathrm{d}t = k_{obsd} = k_2K[X]/(K + [C_2H_4]) \quad (4)$$

consistent with the following mechanism

$$PtL_2(C_2H_4) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtL_2 + C_2H_4 \text{ (rapid equilibrium)} \quad (5)$$

$$PtL_2 + X \xrightarrow{k_2} \text{product } (PtL_2(CH_3)I, \text{ etc.}) \quad (6)$$

where X = CH_3I, $C_6H_5CH_2Br$, or CH_2ICH_2I, $[PtL_2(C_2H_4)]_{tot} = [PtL_2(C_2H_4)] + [PtL_2]$, and $K = (k_1/k_{-1})$, *i.e.*, the equilibrium constant for the dissociation of $PtL_2(C_2H_4)$ according to eq 5. In accord with eq 4, the kinetic data yielded linear plots of $k_{obsd}^{-1}[X]$ *vs.* $[C_2H_4]$ from the slopes of which the values of k_2K, 3.8×10^{-5}, 4.2×10^{-4}, and 7.5×10^{-3} sec^{-1}, were obtained for CH_3I, $C_6H_5CH_2Br$, and CH_2ICH_2I, 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 M^{-1} sec^{-1}, respectively, for k_2. The above value of K implies considerable dissociation of $PtL_2(C_2H_4)$ 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

$$PtL_2(C_2H_4) + C_6H_5C{\equiv}CH \longrightarrow PtL_2(C_6H_5C{\equiv}CH) + C_2H_4 \quad (7)$$

Two distinct reactions were observed. An initial, immeasurably fast, reaction is attributed to the combination of $C_6H_5C{\equiv}CH$ with the PtL_2 initially present in equilibrium with $PtL_2(C_2H_4)$. A subsequent slower reaction obeyed the rate law

$$-\mathrm{d}\ln[PtL_2(C_2H_4)]/\mathrm{d}t = k_1k_2'[C_6H_5C{\equiv}CH]/(k_{-1}[C_2H_4] + k_2'[C_6H_5C{\equiv}CH]) \quad (8)$$

derived for the mechanism

$$PtL_2(C_2H_4) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtL_2 + C_2H_4 \quad (5)$$

$$PtL_2 + C_6H_5C{\equiv}CH \xrightarrow{k_2'} PtL_2(C_6H_5C{\equiv}CH) \quad (9)$$

This is analogous to the mechanism of acetylene replacement in complexes of the type PtL_2(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* $C_6H_5C{\equiv}CH$, 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 $k_2' = 2.8 \times 10^2$ M^{-1} sec^{-1}. The much higher reactivity of $C_6H_5C{\equiv}CH$ (compared with that of CH_3I, $C_6H_5CH_2Br$, or CH_2ICH_2I) toward PtL_2 accounts for the

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