(t-Bu)$_3$P with [(COT)$_2$IrCl]$_2$ (COT = cyclooctene) in the presence of γ-picoline has also been reported[5] very recently. In contrast, with less bulky phosphines which form highly reactive two-coordinate platinum(0) and palladium(0) complexes, tri-*tert*-butylphosphine is reported to form rather inert two-coordinate complexes[6-8] with platinum(0) and palladium(0). Herein we wish to report a novel reaction of tri-*tert*-butylphosphine with hydrated rhodium(III) and iridium(III) trichlorides in which a P-C bond of (t-Bu)$_3$P is cleaved and the complexes *trans*-[(t-Bu)$_2$HP]RhClCO (**1**) and *trans*-[(t-Bu)$_2$HP]$_2$IrCl(CO) (**2**) are formed in almost quantitative yields.

When a mixture of $RhCl_3(H_2O)_3$ (1 mmol) and (t-Bu)$_3$P (5 mmol) was refluxed in dimethylformamide (DMF), under nitrogen, a dark red solution with some suspended solid was formed, initially. After 30 min, a clear yellow solution was obtained which was refluxed for another 2 h. Upon cooling the yellow solution to room temperature and adding methanol, **1** was obtained as a yellow solid in 95% yield, mp 265 °C. A similar reaction of (t-Bu)$_3$P with $IrCl_3(H_2O)_3$ afforded **2** in over 95% yield, mp 270 °C. Both **1** and **2** were characterized by elemental analyses (C, H, Cl, P, Rh, and Ir) and by molecular weight and infrared and NMR spectral measurements. Conductance measurements on 10^{-3} M solutions in nitromethane showed that both **1** and **2** are nonelectrolytes. The molecular weights for **1** and **2** in benzene were found to be 433 and 520, respectively. The infrared spectra of both compounds showed medium-intensity bands at ~2360 and 890 cm^{-1} due to the P-H stretching and P-H bending frequencies,[9] respectively. The CO stretching frequency for **1** and **2** was observed at 1965 and 1940 cm^{-1}, respectively. The ^{31}P NMR spectrum of **1**, in dichloromethane, at −90 °C, showed a doublet (δ 77.5 ppm downfield from external H_3PO_4, J_{P-Rh} = 115 Hz), and the ^{31}P NMR spectrum of **2** showed a single peak (δ 72.7 ppm downfield from external H_3PO_4). Both **1** and **2** have been prepared previously[10] from the reactions of (t-Bu)$_2$Ph following usual preparative methods. The ^{1}H NMR spectra for both compounds, at ambient temperature as well as at low temperatures, were identical with those reported by previous workers.[10]

While the cleavage of P-C bond in the reactions of tertiary phosphines with transition metals leading to the formation of phosphido complexes is well recognized,[11-13] the present report provides the first example of a P-C bond cleavage reaction of a tertiary phosphine resulting in the formation of a secondary phosphine complex. The formation of **1** and **2** was accompanied by the evolution of $H_2C{=}C(CH_3)_2$ which was trapped as $H_2BrC{-}CBr(CH_3)_2$ and characterized by its ^{1}H NMR spectrum. No $H_2C{=}C(CH_3)_2$ was evolved when a solution of (t-Bu)$_3$P in dimethylformanide was refluxed for 3 h. Therefore, the formation of **1** and **2** does not appear to involve the prior formation of (t-Bu)$_2$PH as a consequence of thermal decomposition of (t-Bu)$_3$.

^{1}H NMR measurements on solutions of $RhCl_3(H_2O)_3$ or $IrCl_3(H_2O)_3$ and tri-*tert*-butylphosphine (1:5 mole ratio), in *N,N*-dimethylformamide, indicated the presence of hydrido complexes. The ^{1}H NMR spectra for both rhodium and iridium solutions showed a complex multiplet due to the *tert*-butyl protons. For the rhodium solution, two high-field doublets were observed at δ −24.52 ($^1J_{Rh-H}$ = 5 Hz) and −50.44 ($^1J_{Rh-H}$ = 28 Hz) ppm, respectively. By analogy to the ^{1}H NMR data for the reported rhodium(III) hydrido complexes,[2] the doublet at −24.52 ppm can be due to a six-coordinate monohydrido species $RhHCl_2[(t\text{-}Bu)_3P]_x(DMF)_y$ and the doublet at −50.44 ppm can be due to the pentacoordinate species $RhHCl_2[(t\text{-}Bu)_3P)]_x(DMF)_y$. The failure to observe the splittings due to the P-H spin-spin coupling is not unusual and can be explained in terms of rapid phosphine exchange within each complex. The ^{1}H NMR spectrum of the iridium solution showed a triplet at δ −23.86 ppm ($^2J_{P-H}$ = 16 Hz). By comparison with the ^{1}H NMR data for $[(t\text{-}Bu)_3P)]_2IrH_2Cl_3$,[3] the observed triplet can be associated with a six-coordinate dihydrido complex $[(t\text{-}Bu)_3P]_2IrH_2Cl(DMF)$. Thus, there can be little doubt that the formation of **1** or **2** is preceded by the formation of rhodium(III) or iridium(III) hydrido complexes. However, attempts to isolate the hydride species by precipitation or removal of the solvent and excess phosphine were not successful owing to the formation of oily materials. No evidence for the presence of metallated phosphine[14] in the above solutions was obtained in the ^{31}P NMR spectrum. Further investigations on the reactions of tri-*tert*-butylphosphine with platinum metals are in progress.

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(14) The ^{31}P chemical shifts for the metallated tri-*tert*-butylphosphine occur upfield from the H_3PO_4 external reference, whereas the ^{31}P chemical shifts for free as well as coordinated tri-*tert*-butylphosphine are downfield.[4,5]

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A Model β Turn. Circular Dichroism and Infrared Spectra of a Tetrapeptide[1]

Sir:

Circular dichroism (CD) measurements have been used extensively to evaluate the conformation of proteins and polypeptides in solution.[2-4] For accurate determinations of conformation, the optical parameters of all known secondary structures must be known. The evaluation of conformation of proteins to date has been based on the α-helical, β sheet and random conformational optical parameters deduced from either synthetic polypeptides,[2] or from five proteins of known structure.[3] However, the β turn has been neglected because the parameters were unknown, although the β turn or β bend has been recognized as playing an important role in globular proteins:[5] the average frequency of amino acid residues in β turns is 32%.[9]

The β turn is a structural feature involving four consecutive residues where the polypeptide chain folds back on itself, with hydrogen bonding between the CO group of the first residue and the NH group of the 4th residue. Only recently have the exact parameters been evaluated for the various types of β turns,[5a,c,6] their presence tabulated in proteins,[5] and their optical activity theoretically evaluated.[7] β bends have been classified into 11 types,[5a,c] but types I and II are found most

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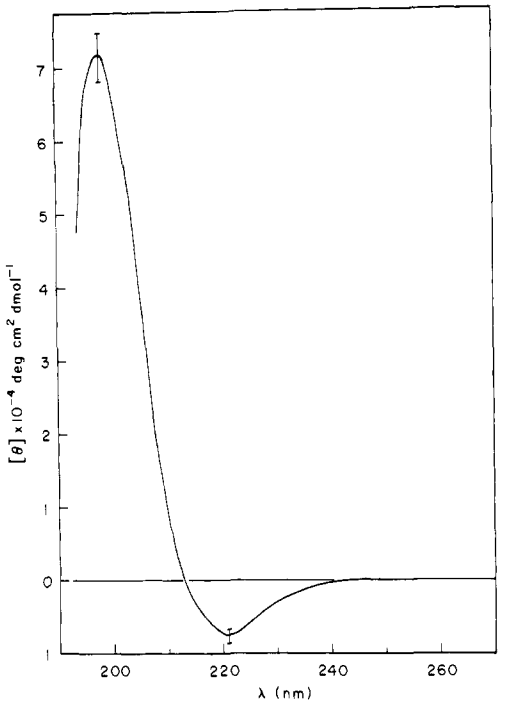

Figure 1. Circular dichroism spectrum of Cbz-Gly-L-Ser-(*O*-Bu^t)-L-Ser-Gly-*O*-stearyl ester in cyclohexane: concentration, 0.116 ~ 0.056 mg/mL; 1-mm cell; temperature, 23 °C.

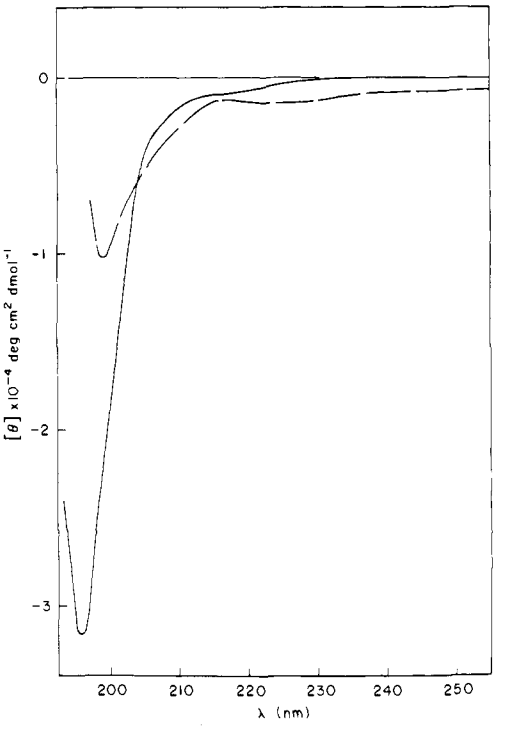

Figure 2. Circular dichroism spectra of Cbz-Gly-L-Ser-(*O*-Bu^t)-L-Ser-Gly-*O*-stearyl ester in cyclohexane and MeOH: cyclohexane, 1.40 mg/mL (—); MeOH, 0.2 mg/mL (— — —); 1-mm cell; temperature, 23 °C.

predominately in proteins.[5g] The CD spectrum reported[8] for the polytetrapeptide (Val-Pro-Gly-Gly)$_{40}$, a repeating unit of elastin, is purported to be that of a series of β turns.

We wish to report the optical properties of a tetrapeptide, Cbz-Gly-L-Ser-(*O*-Bu^t)-L-Ser-Gly-*O*-stearyl ester, which is believed to exist as a β turn under specific conditions. This peptide was synthesized because of the predicted high probability of a β turn for these residues in their respective positions, as well as the fact that four such peptides are found as type-I β turns in proteins.[9]

The strategy was as follows. An unblocked or simply blocked tetrapeptide, soluble in H_2O, would not be expected to form a β turn because of competition from the aqueous media, as was shown for other tetrapeptides.[10] Therefore, a derivative was chosen which would solubilize the tetrapeptide in an organic nonpolar solvent, e.g., cyclohexane. The N terminus was blocked by an *N*-carbobenzyloxy group, while the carboxyl function was esterified with stearyl alcohol, which yielded the desired solubility properties. The detailed synthesis will be published elsewhere.

The circular dichroism spectrum of this tetrapeptide, in cyclohexane, is shown in Figure 1. This measurement was made with a Cary 60 spectropolarimeter with a CD attachment, No. 6001 (under a nitrogen atmosphere). The CD extrema are seen at 198 nm, $[\theta]_{198} = +71\,900 \pm 4000$ and at 221 nm, $[\theta]_{221} = -7800 \pm 800$ with a crossover point at 213 nm, where $[\theta]$ is expressed in molar ellipticity (deg cm^2/dmol) and calculated per mole of peptide residue. Although this CD curve resembles those of the β-pleated sheet,[11] it is clearly evident that the peak and trough are distinctly shifted, and of a different magnitude. This curve is similar to those predicted by Woody[7] for the type I and II β bend of Venkatachalam,[6] where the peak and trough were predicted to be at ~205 and 225 nm, respectively. However, the magnitude of the ellipticities were found to be greater than those predicted (−5000, + 30 000). Thus this spectrum is associated with that expected of a type I or type II β turn. An interesting concentration dependence on the magnitude of the CD values was found for the tetrapeptide in cyclohexane. At concentrations from 2.18 mg/mL to 0.545 mg/mL the CD spectra indicated the random conformation; from 0.310 to 0.28 mg/mL the CD values at $[\theta]_{198}$ and $[\theta]_{221}$ increased. From 0.28 to 0.056 mg/mL the $[\theta]_{198}$ and $[\theta]_{221}$ leveled off at the reported constant value. This behavior would suggest that at higher concentrations there was an *inter*molecular association of a random type, but in dilute solution only *intra*molecular hydrogen bonding between residues 4 and 1 occurred, producing a β bend. The CD spectrum of the random conformation of the tetrapeptide is shown in Figure 2. At high concentrations (1.40 mg/mL) in cyclohexane $[\theta]_{196} = -31\,540$, while in MeOH at lower concentration (0.20 mg/mL) $[\theta]_{198} = -10\,020$ was obtained. The shape of both curves is similar to the random conformation of polypeptides and proteins;[15] at higher concentrations in cyclohexane random aggregation probably occurs yielding the larger values, while in MeOH the spectrum is due to the unassociated species.

In an attempt to confirm the conformational assignment of the tetrapeptide, infrared spectroscopy was carried out as shown in Figure 3. The spectra were obtained on a Perkin-Elmer 621 spectrophotometer. As seen in Figure 3c, when this peptide was measured as a film cast from dilute cyclohexane solution (0.06 mg/mL) the following bands were observed: 1750 cm^{-1}, C=O stretching of the ester; 1730 cm^{-1}, C=O stretching of the urethane; 1695, 1665, 1635 cm^{-1}, amide I; 1550, 1552 cm^{-1}, amide II; and 3295 and 3260 cm^{-1}, amide A region bands. The assignment of the amide I bands is as follows: 1695 cm^{-1}, antiparallel β sheet; 1665 cm^{-1}, random coil (or helix); and 1635 cm^{-1}, β sheet.[12] An absorption band at ~3410 cm^{-1} is that expected for a free NH vibration,[13] but when hydrogen bonded is shifted to lower frequency. Thus the two bands at 3295 and 3260 cm^{-1} must be those observed for the NH-hydrogen-bonded species, as would be expected for a 4-1 hydrogen bond in a β turn.

As was found for the CD spectra, the IR spectra of films were found to be dependent on the concentration of the solutions cast into films. As shown in Figure 3a, the film cast at the higher concentration has a band at 3295 cm^{-1}, weak bands at 1695 and 1665 cm^{-1}, and a strong band at 1635 cm^{-1}. As the film is cast from more dilute solution, the bands at 3260 and

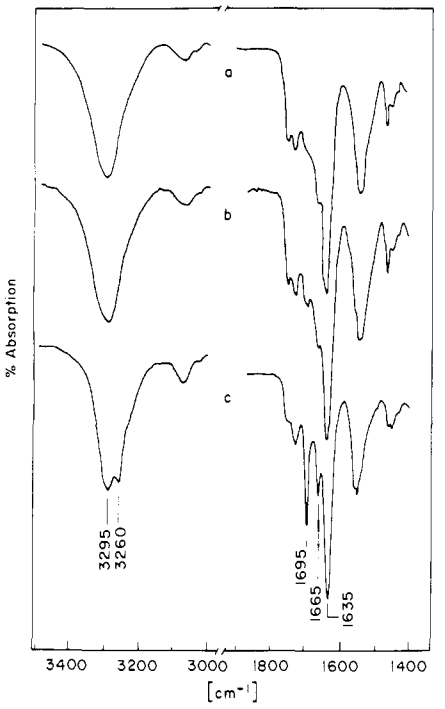

Figure 3. Infrared spectra of films of Cbz-Gly-L-Ser-(*O*-Bu^t)-L-Ser-Gly-*O*-stearyl ester cast from various concentrations in cyclohexane: (a) 3.54 mg/mL; (b) 0.290 mg/mL; (c) 0.060 mg/mL.

1695 cm^{-1} became more pronounced (Figure 3b,c). As the 1695-cm^{-1} band increases, the 1665-cm^{-1} band decreases while simultaneously there is a greater splitting between the 3295- and 3260-cm^{-1} bands. As the 1695-cm^{-1} absorption band is that found for the antiparallel β sheet, it would also be expected to exist for the β bend. Thus, under the conditions of high dilution, where the maximum CD values were observed, one finds a splitting of the amide A band at 3295 and 3260 cm^{-1} and in the amide I region one finds an extremely large 1695-cm^{-1} band in comparison with an extremely small 1665 and a large 1635-cm^{-1} band. Therefore, it is suggested that this IR spectrum is that of a β bend, while at higher concentrations intermolecular association exists. It appears that the ratio of the 1695-cm^{-1} band to the 1635-cm^{-1} band is larger in the β bend than that found in the antiparallel β sheet. For the tetrapeptide *N*-Cbz-Gly-L-Pro-L-Leu-Gly, which has been shown to be a type I β bend by x-ray crystallography,[14] when examined in Nujol mulls, the ratio of (r) 1687/1638 = 0.83. For the tetrapeptide studied therein, *N*-Cbz-Gly-L-Ser-(*O*-Bu^t)-L-Ser-Gly-*O*-stearyl ester, the ratio 1695/1635 = 0.68 was observed. For antiparallel β sheets, lower ratios of these two bands have been reported: poly-(L-Glu-ONa), β form, r = 0.41;[15] poly(L-Thr), r = 0.29;[11] (L-Glu-L-Val-L-Glu)$_n$, r = 0.10;[16] and (L-Glu-L-Glu-L-Val-L-Glu)$_n$, r = 0.13.[16] Thus, the magnitude of the 1695/1635 ratio may be indicative of β bends.

The infrared spectrum of a Nujol mull of crystalline *N*-Cbz-Gly-L-Pro-L-Leu-Gly, known to exist as a type-I β bend in the crystal,[14] showed the following bands: amide A region, 3360 (s), 3330 (m), and 3270 cm^{-1} (m); amide I region, 1687 (s), 1655 (m), and 1638 cm^{-1} (s). Thus the similarity of the IR spectrum shown in Figure 3c with that found for the type-I β bend establishes the conformation of the tetrapeptide synthesized therein.

On the basis of the IR spectra, the probability of β-turn formation for this sequence,[9] Gly-L-Ser-L-Ser-Gly, and the similarity of the CD spectrum to that calculated for a β bend,[7] it is believed that a type I β turn exists at high dilution in cyclohexane. Thus, the CD spectrum shown in Figure 1 is that for the type-I β turn. As 42% of identified β turns in proteins[9] are of the type-I β turn, and another 15% of β turns are found to be type-II β turns,[9] a total of 57% of β turns in proteins might be expected to display this spectrum, as Woody[7] has calculated that both type-I and type-II turns would display similar CD spectra. It may now be possible to calculate the conformation of proteins in solution with greater accuracy utilizing CD measurements if this β-turn spectrum is used in combination with those of other known conformations. Such studies are in progress.

While this work was in progress, the CD spectrum of another material believed to be in the β-turn conformation, poly(L-Ala$_2$Gly$_2$) was published,[17] which was similar to that calculated by Woody,[7] but with much larger magnitudes. As the extrema (227, 207.5 nm) are slightly displaced from those reported herein, as well as having lower magnitudes, it is not known whether this is the spectra of a different β turn, or whether there are interactions between β turns. Further research will be necessary to evaluate these possibilities.

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Generation of Stable Acidic Solutions of Copper(III) Chelates from Basic Copper(II) Solutions

Sir:

The discovery by Margerum and co-workers[1-3] of water-stable copper(III) chelates containing peptide linkages has generated much interest especially considering the proposed role of copper(III) in galactose oxidase and tyrosinase.[4-5] The major problem in the study of copper(III) chelates is their relative instability in neutral and basic solutions. In Table I it is quite apparent that, as the pH is raised, the decomposition

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