residue becomes available and the tail-linked residue becomes either highly deshielded (in the presence of Pr^{3+}) or shielded (in the presence of Eu^{3+}). These effects are attenuated for other residues which are successively removed from the tail-linked residue, thus allowing the enumeration of at least two (and in favorable cases, even three) residues from the tail side. These measurements, together with the original lanthanide ion induced shifts observed without added base and the relatively unaffected shift of the "middle" residue, allow the sequential determination of hexa- or even heptapeptides. Additionally, in those cases (*e.g.*, pentaglycine and others) where the sequence could be stated unambiguously by the acid-base titration method,[1] the consecutive addition of lanthanide salts affirmed fully the assignments of the residues as pointed out earlier (see also Figure 3).

Work is in progress to check and optimize the nmr method through systematic investigation of other La^{3+} ions, solvents and mixed polypeptides, and we plan to submit a full account of our findings shortly. Some drawbacks at this stage are already apparent. One difficulty is that the addition of base often causes pronounced broadening of the absorption patterns. Another is that solubility problems are encountered with peptides containing more than five amino acid residues. Thus it will be necessary to consider other potential (binary) solvent (systems) which do not themselves coordinate too strongly with LSR. Further, the occurrence of multifunctional amino acid residues may cause difficulties arising from the presence of multiple potential ligand sites. Thus, at the present stage of our investigation, we are not overly optimistic that the nmr method discussed herein can be universally employed as a nondestructive method for sequential analyses of oligopeptides. The existence of Fourier transform techniques permits the utilization of much smaller quantities of material then used in conventional CW measurements, thus rendering the method interesting in principle for biological purposes.

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Stereochemistry of the Rhodium-Catalyzed "Oxo" Reaction

Sir:

In spite of the great deal of work done on the "oxo" reaction during the last decades,[1] little information is available on the stereochemistry of the addition of the formyl group and hydrogen to the double bond. Although cis addition is generally assumed in the cobalt-catalyzed reaction,[2] conclusive evidence has been presented only in one case[3] and that did not involve an alkene. No information whatsoever is available on the steric course of the rhodium-catalyzed hydroformylation.

We have investigated the hydroformylation of (*E*)-(**1**) and (*Z*)-3-methyl-2-pentene (**2**) in the presence of hydridocarbonyltris(triphenylphosphine)rhodium.[4] Both reactions were carried out as follows: 5 g of olefin and 80 mg of catalyst in 50 ml of benzene were treated at 80° with CO and H_2 (1:1; initial pressure 80 atm). The reactions were stopped when the drop of pressure (25 atm) indicated 50% of conversion. The residual olefins and the products were analyzed by gas chromatography-mass spectrometry (Perkin-Elmer vapor fractometer 990, Hitachi mass spectrometer RMU-6L) against standard samples. The compositions of the reaction mixtures are reported in Table I. The diastereomeric composition of the main products was determined after conversion of the aldehydes into the methyl esters of the corresponding acids;[5] details on the experimental procedure and on the analytical conditions are given elsewhere.[6] No saturated hydrocarbon was detected in the reaction mixture.

Table I. Compositions (%) of Reaction Mixtures

Reaction mixture	Starting olefin (*E*)-3-Methyl-2-pentene (**1**)	 (*Z*)-3-Methyl-2-pentene (**2**)
Products		
2,3-Dimethylpentanal	86	85
3-Ethylpentanal	3	3
4-Methylhexanal	11	12
Residual olefins		
1	94	8
2	6	92
2,3-Dimethylpentanal		
Erythro	6	92
Threo	94	8

As isomerization accompanying the hydroformylation occurs only to a small extent, the stereochemistry of the reaction is clearly evident from the above results, indicating overwhelming cis addition in both cases.

Although the isomeric composition of the residual olefins suggested that cis-trans isomerization might be responsible for the incomplete diastereomeric purity of the main products, more rigorous evidence was needed to determine the degree of the stereospecificity of the hydroformylation. Therefore, a deuterioformylation of **1** was carried out under the conditions used in the previous hydroformylation,[7] the reaction mixture composition at 50% conversion being in both cases the same. The deuterium content in the residual olefins and in the methyl esters derived from the reaction products[5] was determined by mass spectral analysis: unreacted **1** was more than 90% undeuterated, while the

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(1) Extensive reviews are available on the subject; *e.g.* (a) J. Falbe, "Synthesen mit Kohlenmonoxyd," Springer-Verlag, Berlin, 1967; (b) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, Academic Press, New York, N. Y., 1967; (c) A. J. Chalk and R. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968).

(2) M. Orchin and W. Rupilius, *Catal. Rev.*, **6**, 85 (1972).

(3) A. Rosenthal, *Advan. Carbohyd. Chem.*, **23**, 60 (1968).

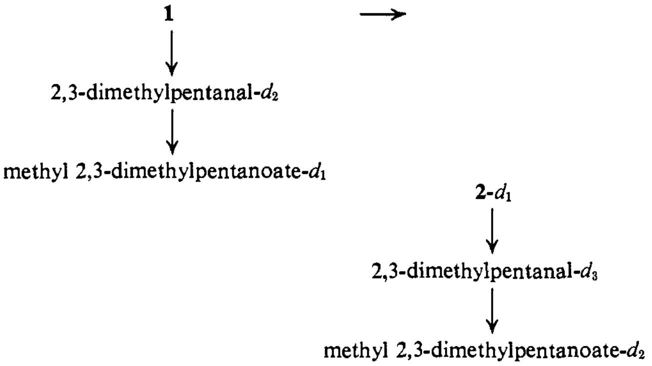
(4) C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970).

(5) P. Pino, S. Pucci, F. Piacenti, and G. Dell'Amico, *J. Chem. Soc. C*, 1640 (1971).

(6) A. Stefani, *Helv. Chim. Acta*, **56**, 1192 (1973).

(7) An incorporation of one deuterium atom was found by P. Taylor and M. Orchin (*J. Organometal. Chem.*, **26**, 389 (1971)) in the dimethyl maleate-dimethyl fumarate isomerization in the presence of stoichiometric amounts of $DCo(CO)_4$.

isomerized olefin **2** was substantially monodeuterated (>95%); methyl *threo*-2,3-dimethylpentanoate was more than 90% monodeuterated and the erythro isomer contained two deuterium atoms. Clear evidence was thus provided that **1** and **2** are precursors of individual diastereoisomers, *i.e.*, threo and erythro respectively.



The above results show not only that a cis addition of hydrogen and formyl group occurs in the hydroformylation of both cis and trans internal olefins, but also that the stereospecificity of the reaction is indeed very high. Assuming that the three isomeric aldehydes arise from different intermediates, the stereospecificity of the hydroformylation of the internal double bonds can be considered practically complete.

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Synthesis and Characterization of Novel Pentagonal Bipyramidal Complexes of Iron(II), Cobalt(II), and Zinc(II)

Sir:

We report the synthesis and characterization of the first pentagonal bipyramidal complexes of Fe(II), Co(II), and Zn(II) using the planar pentadentate ligand 2,6-diacetylpyridenebissemicarbazone, DAPSC. Examples of heptacoordination in first-row transition metals are limited, at present, to the heptacyanovanadate ion,[1] $V(CN)_7^{4-}$, to hydrated EDTA complexes of Mn(II)[2] and Fe(III),[3] and a macrocyclic complex of Fe(III).[4] The vanadium complex is the only reported cyanide complex of a first-row transition element with a coordination number greater than six.[5] The flexible nature of EDTA was not expected to produce seven-coordinate molecules routinely. In the case of the macrocycle, the complex was originally postulated as octahedral[6] and apparently was not allowed to react with other metals. However, for a systematic study of seven coordination, it was essential to design a ligand that consistently would produce pentagonal bipyramidal complexes. Therefore, as part of a study of planar pentadentate ligands, we treated an alcohol solution of diacetylpyridine and the appropriate metal chloride with semicarbazide hydrochloride. After slow evaporation of solvent we obtained crystalline products corresponding to the stoichiometry $DAPSC \cdot MCl_2 \cdot 3H_2O$,[7] where M is Fe, Co, Ni, or Zn, which suggested a pentagonal bipyramidal metal complex.[8] The unusual nature of this type of coordination for first-row transition elements prompted an X-ray crystal structure study of these complexes, which has confirmed that they are indeed heptacoordinate.

The Fe(II), Co(II), and Zn(II) complexes are isomorphous. The crystals are monoclinic with cell dimensions of a = 18.096, 17.968, 18.038 Å; b = 13.11, 13.139, 13.112 Å; c = 8.061, 8.052, 8.066 Å; and β = 99.76, 99.86, 100.28° for the Fe(II), Co(II), and Zn(II) complexes, respectively. The densities calculated for four molecules of $DAPSC \cdot MCl_2 \cdot 3H_2O$ per unit cell are 1.615, 1.636, and 1.655 g cm^{-3} compared with 1.62, 1.63, and 1.63 g cm^{-3} found by flotation for the Fe, Co, and Zn complexes. The systematic extinction suggested that the space group was either *Ia* or *I*2/*a* (nonstandard setting of *Cc* or *C*2/*c*), with the former being favored by the intensity statistics. The successful analysis carried out in *Ia* confirmed this choice.

Intensity data for all three complexes were measured using a Syntex P$\bar{1}$ diffractometer with a variable speed θ–2θ scan technique. The data for Fe(II) and Co(II) complexes were obtained using graphite monochromatized Mo Kα radiation but the Zn(II) data were obtained with Ni-filtered Cu Kα radiation. The Zn(II) complex was solved by the heavy-atom technique, with subsequent Fourier syntheses to determine the light atom positions. All electron density maps suggested that the two axial ligands were not both chlorine atoms as would be required in space group *I*2/*a* with four molecules per unit cell. The refinement was by least-squares techniques to a final *R* of 0.059 for the 1172 observed reflections used in the analysis. The Fe(II) and Co(II) complexes were found to be isomorphous, and least-squares refinement used the Zn(II) coordinates as a starting point. The final *R* values were 0.040 for 1504 observed reflections for the Fe(II) complex and 0.039 for 1518 observed reflections for the Co(II) case.

The pentagonal bipyramidal nature of these complexes is easily seen in Figure 1, which is an ORTEP drawing obtained using the parameters from the Co(II) complex. The five donor atoms N1, N2, N5, O1, and O2 form an approximately planar pentagon around the metal ion, with a chlorine atom and a water molecule in the axial positions. The deviations of the five donor atoms from planarity are identical in the three complexes. If N1 is considered to be on the plane, N2 is above and N5 below the plane by about 0.07 Å and O1 is below and O2 is above the plane by about 0.01 Å. The nature of these distortions is not understood since uncomplexed semicarbazones also show slight deviations from planarity.[9]

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(7) The chemical analyses were in good agreement with this formulation which was further confirmed by the X-ray studies.

(8) The case of Cu(II) is more complex with two different products resulting from the reaction. These studies are being pursued in more detail.

(9) D. V. Naik and G. J. Palenik, unpublished results.