in which the aqua ligand can be replaced by a variety of coordinating anions.[6,10]

Copper-substituted insulin has been crystallized and studied in detail[11] via X-ray diffraction and ESR spectroscopy under T-state conditions (octahedral Cu(II) coordination). From these studies it has been concluded that Cu(II)-insulin crystals are isomorphous with Zn(II)-T_6 crystals and that the crystal structures of copper and zinc insulin are essentially the same. Our results indicate that in solution the Cu(II)-insulin hexamer[12] undergoes the T_6 to R_6 conformational transition in a manner analogous to that established for the Co(II) and Zn(II) hexamers, producing a Cu(II)-R_6 species upon the addition of a methanol solution of PFTP. This gives rise to an intense blue color, which is attributable to the PFTP complex of the Cu(II)-R_6 hexamer[13] (compound **1**). The UV-visible absorption spectrum of **1** (Figure 2, Table I) displays an intense band at 626 nm and is similar to those reported for blue copper proteins. The ESR spectrum of **1** (Figure 3)[14] displays a hyperfine coupling constant $A_{\parallel}$ of 80×10^{-4} cm^{-1}, a value significantly lower than those usually reported for low molecular weight copper(II) complexes (viz., $A_{\parallel} = 130\text{-}220 \times 10^{-4}$ cm^{-1}).[1e]

Cobalt(II) substitution is well recognized to give an extremely sensitive spectroscopic probe of the geometrical and donor characteristics of the metal chelate sites in many metalloproteins.[15] The UV-visible absorption spectrum obtained for the Co(II)-R_6 complex of PFTP (compound **2**) is given in Figure 2 and Table I. There is an extraordinary resemblance between this spectrum and those of the Co(II)-substituted blue copper proteins, azurin (Table I), plastocyanin, and stellacyanin.[16] Spectral data for the Cu(II)-R_6 and Co(II)-R_6 complexes obtained with several thiophenol derivatives (compounds **3**–**6**) are presented in Table I. The spectral variation displayed by this series shows that substitutions in the aromatic ring of thiophenol alter the donor properties of the coordinated thiolate sulfur atom and thereby influence the spectroscopic features of the copper(II) center.

Collectively, the present results strongly suggest that the peculiar spectra exhibited by **1** arise from the combination of copper(II)–thiolate (PFTP) ligation in conjunction with the ligand field imposed by the His-B10 site of the R_6 insulin hexamer. According to all the spectroscopic criteria thus far examined, this particular donor arrangement evidently generates a chemical environment in which the electronic energy states of the copper(II) ions in **1** are very similar to those of the copper(II) ions in blue copper proteins.

We conclude that complexes formed via the interaction of thiophenol derivatives with the Cu(II)-R_6 insulin hexamer provide a useful model system through which the spectrochemical features of the blue copper center may be systematically probed.[17] Current investigations[18] indicate that similar experiments performed using copper(II)-substituted carbonic anhydrase manifest spectroscopic information that will enhance these studies.

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(12) Solutions of M(II)-R_6 were prepared as described in ref 6 by using 25 mM Tris-ClO_4^- buffer, pH = 8.0. Insulin concentrations were determined from the absorbance measured at 280 nm ($\epsilon_{280} = 5.7 \times 10^3$ per insulin subunit, MW 5800).

(13) M-R_6-thiolate complexes were prepared by using a M:thiolate ratio of 1:1.1. Solutions of **1** gradually faded to a pale blue color over a period of approximately 30 h. This bleaching is indicative of slow reduction to Cu(I).

(14) The ESR spectrum of Figure 3 displays a minor feature at 2640 G. Control experiments indicate that this feature is attributable to a small fraction of T_6 complex present in the $T_6 \rightleftharpoons R_6$ equilibrium.

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Ligand-Induced Selective Stabilization of the Anti Isomer in (η^3-Allyl)palladium Complexes: An Attempt To Control the *E*–*Z* Stereochemistry in Palladium-Promoted Allylic Substitutions

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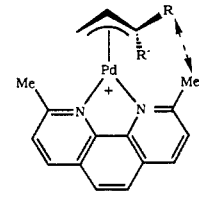
Except in special cases, (η^3-allyl)palladium complexes tend to adopt a syn configuration (**s**), while the less stable anti isomer (**a**) is generally present in less than 10%.[1] It appeared to us that a rigid bidentate ligand, shaped to "embrace" the metal as in **1**, should interfere more sterically with a syn substituent, leading to a preference for the anti configuration.[2] Provided isomerization



1

a R = H, R' = Me
s R = Me, R' = H

is sufficiently fast, this offers the possibility of obtaining *Z* products in palladium-promoted reactions of allylic substrates, irrespective of the configuration of the starting material. Following this idea, we prepared complexes of general formula Pd(N-N)(CH_2–CH–CRR')]$^+$ (**1**, R = H, R' = Me; **2**, R = H, R' = Et; **3**, R = H, R' = *n*-Pr; **4**, R = H, R' = *i*-Pr; **5**, R = Me, R' = $CH_2CH_2CH{=}CMe_2$),[3] from the η^3-allyl-chloride complexes, $AgBF_4$, and 2,9-dimethyl-1,10-phenanthroline (dmphen) using established procedures.[4] Except for the geranyl-neryl complex **5**, which has a disubstituted allyl group, the syn isomer was indeed the less stable, and at equilibrium, the anti/syn ratio was about 70/30. The pure syn complex could be obtained by addition of

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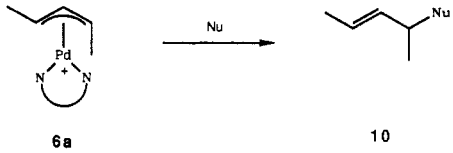
Table I. Stoichiometric and Catalytic Allylic Substitutions Using 2,9-Dimethyl-1,10-phenanthroline Palladium Complexes

starting material (% isom purity)	nucleophile	products, % 7	8	9
1s[a] (95)	$^-C(Me)(COOEt)_2$	94	1	5
1a[a] (95)		7	37	56
1s[b] (92)	$NHMe_2$	70	10	20
1a[c] (95)		6	12	82
(*E*)-MeCH=CH-CH_2OAc[d] (98)	$^-C(Me)(COOEt)_2$	95	1	4
(*Z*)-MeCH=CH-CH_2OAc[d] (53)		45	21	34

[a] Stoichiometric reaction in DMF, counterion fluoroborate, argon atmosphere, 0 °C, 2 equiv of sodium diethyl methylmalonate. [b] Stoichiometric reaction in H_2O, counterion trifluoroacetate, 0 °C, 0.1 mmol/mL, 5 equiv of Me_2NH, 5 equiv of NaCN added after 30 s, 45% reacted. [c] As above; 35% reacted. [d] Catalytic reaction in DMF, argon atmosphere, 20 °C, 1 h, 0.2 mmol/mL substrate, 1% Pd catalyst (1), 4% dmphen, 2 equiv of sodium diethyl methylmalonate.

diethyl ether and rapid crystallization immediately after preparation while the anti complex could be crystallized from the equilibrium mixture. The same anti/syn equilibrium ratio was observed for all terminally monosubstituted allylic groups, indicating that the destabilization of the syn configuration by dmphen is general.[5] In order to determine the chemical consequences of the stereochemistry of the η^3-allyl group, essentially pure (~95%) syn and anti complexes, **1s** and **1a**, were reacted separately with the anion of diethyl methylmalonate. The syn complex gave essentially pure *E* product **7**, and the anti complex gave the *Z* product **8** together with the regioisomer **9** in the ratio 37/56 (Table I). Essentially the same product pattern was observed when the hexenyl complex **3** was used, suggesting that this is a general behavior of complexes of monosubstituted allyl groups. We also prepared the complex $[Pd(dmphen)(MeCH{-}CH{-}CHMe)]^+BF_4^-$ (**6**), which gave an 83/17 equilibrium mixture of syn,anti (**6a**) and syn,syn (**6s**) isomers, respectively. When this was reacted with the anion of methylmalonate, only the *E* product **10** could be detected, confirming a higher relative reactivity at the anti substituted carbon. The effect of a different nucleophile on the



6a **10**

N⌣N = dmphen, Nu = $^-C(Me)(COOEt)_2$

product pattern was studied by reacting the crotyl complexes **1a** and **1s** with dimethylamine. In order to minimize isomerization of the primary products,[6e] the reaction was performed in water solution at 0 °C by using the trifluoroacetate salts of **1a** and **1s** and quenching the reaction after 30 s with an excess of sodium cyanide. Despite appreciable isomerization also under these conditions, the trends from addition of malonate were confirmed, i.e., retention of *E* and *Z* stereochemistry and preference for reaction at the secondary position in the case of the anti isomer **1a**. The latter result could be a problem in catalytic reactions, but it obviously represents a novel concept for regiocontrol.

Although pyridine type ligands are generally not useful in catalytic reactions,[6] a few alkylations of (*Z*)- and (*E*)-2-butenyl acetates were performed, with a palladium dmphen as catalyst. Unexpectedly, both complete retention of configuration (Table I) and faster reaction than with $Pd(PPh_3)_4$ were observed, perhaps due to more rapid oxidative addition.

These results show that the initial concept of stereocontrol is correct. However, truly catalytic conversion of *E* substrates into *Z* products requires further studies of ways to influence the relative rates of isomerization and nucleophilic attack. Such studies are under way in our laboratories.

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Supplementary Material Available: Elemental analyses and NMR spectral data of compounds **1a** and **1s** (1 page). Ordering information is given on any current masthead page.

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$[(MeC_5H_4)_3U]_2[\mu\text{-}1,4\text{-}N_2C_6H_4]$: A Bimetallic Molecule with Antiferromagnetic Coupling between the Uranium Centers

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Antiferromagnetic coupling of electron spins on two or more metal centers that are connected by bridging ligands, referred to as indirect coupling or superexchange coupling, is a topic of considerable interest in d-transition-metal chemistry.[1] In the f-block metals, a few examples of antiferromagnetic exchange coupling have been observed in solid-state compounds with extended lattices such as UCl_3[2a,b] and $EuCl_2$,[2c] where the ordering temperatures are ca. 22 K and 1.6 K, respectively. Antiferromagnetic coupling has been observed in a molecular lanthanide system, $Cp_4Dy_2(\mu\text{-}Br)_2$, with an ordering temperature of 6 K, though no coupling was observed in $Cp_4Er_2(\mu\text{-}Br)_2$, $Cp_4Yb_2(\mu\text{-}Br)_2$,[3a-d] or $[(Me_5C_5)_2Yb]_2(\mu\text{-}E)$ where E is O, S, Se, or Te.[3e] Recently, inelastic neutron scattering experiments have been interpreted in terms of electron exchange coupling in the confacial bioctahedral compounds $Cs_3M_2Br_9$ where M is Yb, Tb, or Ho.[3f,g] In the actinide series, no examples of coupling have been documented in molecular systems; the U(IV) compounds $[(MeC_5H_4)_3U]_2(\mu\text{-}E)$[4a] and $\{[(Me_3Si)_2N]_3U\}_2(\mu\text{-}E)$[4b] where E is

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