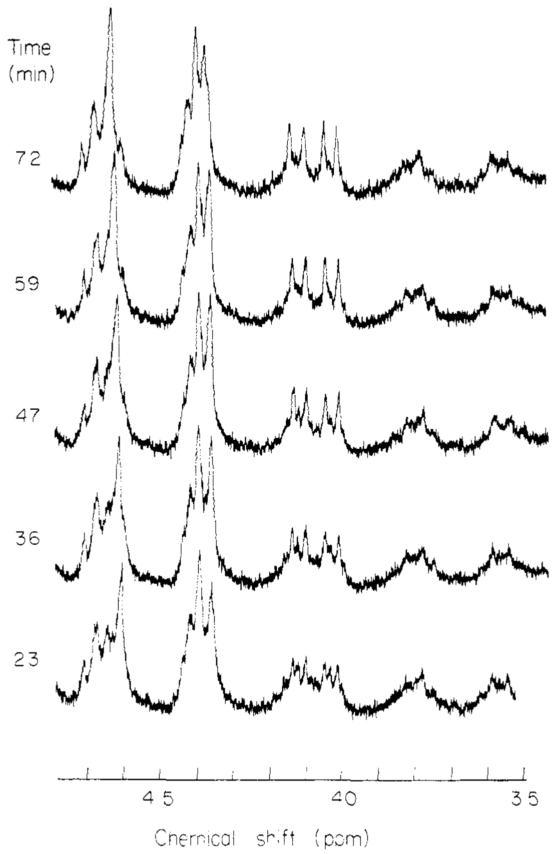

Figure 1. The α-proton region of the 220-MHz spectrum of angiotensin II during deuterium exchange. As a function of time the two resonances at 4.04 and 4.13 ppm simplify as they are no longer coupled to pronated amides.

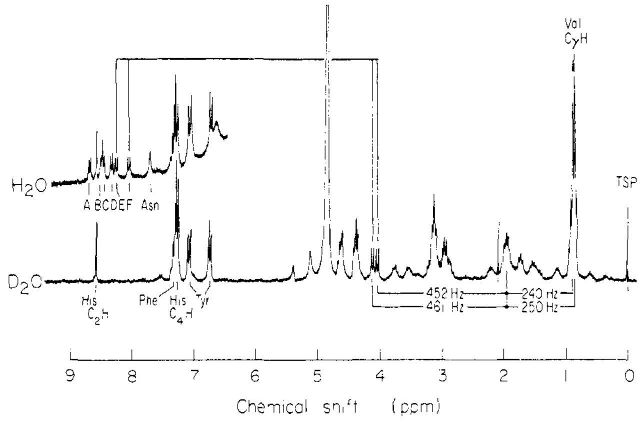

Figure 2. The 220-MHz spectrum of angiotensin II in D_2O and H_2O at pH 2.5 and 17°.

hanced rate of base-catalyzed proton exchange as it was not observed 4.5 min after initiating the deuterium exchange experiment in Table I. In addition, it begins to broaden earlier than any other amide resonance as either the pH or the temperature is increased. It can therefore be assigned as the N-terminal amide of Arg_2 by the known exchange characteristics of N-terminal peptide amides.[7] A partial pH profile of the chemical shift of resonance B assigns it to the amide of His_6. The pH profile of resonance D identifies it as the amide proton of Phe_8. By elimination, resonance C can be assigned to the amide proton of Tyr_4 as is summarized in Table I.

The observation of the two slowly exchanging amide protons in Asn_1Val_5 angiotensin II is in agreement with tritium–hydrogen exchange results.[2] Assignment of these protons to the valines rules out the β-turn model, at least in water since it requires a slowly exchanging histidine amide. The observed half-life of 16 min for the exchange of the amide of Tyr_4 is longer than the value of 6–8 min that can be predicted from published data.[7] A shielding of the amide of Tyr_4 could occur from a folding of the C-terminal end of the peptide chain in a conformation similar to the model proposed by Fermandjian, *et al.*,[8] on the basis of circular dichroism, infrared, and Raman studies. The assignment of the slowly exchanging amides to Val_3 and Val_5 is in disagreement with the nmr findings of Weinkam and Jorgensen[9] and Fermandjian, *et al.*,[10] unless a different conformation results from Me_2SO. The data strongly support the proposed γ-turn conformation of angiotensin II in aqueous solution. This folding pattern has been proposed as the most stable conformation in solution as well as the most interesting one pharmacologically.[1,2] Comparative studies in this laboratory with the C-terminal hexapeptide fragment of angiotensin II and with angiotensin I provide evidence for similar conformations, with varying degrees of stability, of all three peptides in aqueous solution.[11]

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trans-Hydridodinitrogenbis-[1,2-bis(diphenylphosphino)ethane]rhenium(I)

Sir:

Although a substantial number of dinitrogen complexes have been characterized, only a few of these also contain hydrogen bonded to the metal atom. The known hydridodinitrogen complexes are so far restricted to group VIII metals (Fe, Co, Ru, and Os) and tungsten. In the present communication we report *trans*-$ReH(N_2)(dppe)_2$ (dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), the second hydridodinitrogen complex outside of group VIII. Interest in this compound is enhanced by its ability to undergo a variety of reactions. We report examples of protonation at the metal, oxidative addition with loss of N_2, reaction of the Re–H bond with halocarbons, and simple replacement of dinitrogen. Taken together these represent a novel chemistry for a rhenium complex. Similar reactions have not

Table I. Selected Ir and Nmr Absorptions of $ReH(N_2)(dppe)_2$ and Some of Its Reaction Products

No.	Compound	ν(Re–H),[a] cm^{-1}	ν(functional group),[a] cm^{-1}	τ(Re–H)[b]	*J*(P–H), Hz	H/Re[c]
I	$ReH(N_2)(dppe)_2$	1818 (w)	2006 (vs)[d]	19.94 (q)[e]	20	0.98
III	$[ReH_2(N_2)(dppe)_2]BF_4$	*f*	2118 (vs)[d]	19.40 (q)[g]	17	1.88
IV	$ReHCl_2(dppe)_2 \cdot C_6H_6$	*f*	280, 250 (w)[h]	18.39 (tt)[i]	16, 71	0.93
V	$ReI(N_2)(dppe)_2$		1988 (vs)[d]			
VI	$ReBr(N_2)(dppe)_2$		1978 (vs)[d]			
VII	$ReH(C_2H_4)(dppe)_2$	1910 (w)	*j*	16.92 (q)[e]	21	1.10
VIII	$ReH(CO)(dppe)_2$	*k*	1843 (vs)[l]	16.21 (q)[m]	21	0.99

[a] Measured on pressed CsI disks; w = weak, m = medium, s = strong, vs = very strong. [b] q, quintet; tt, triplet of triplets. [c] Average value obtained from comparison of the area under the Re–H high-field lines with the area of the methylene proton line of $Ph_2PCH_2CH_2PPh_2$. [d] $\nu(N\equiv N)$. [e] ~5% solution in CS_2. [f] The ν(Re–H) bands are very weak and cannot, with confidence, be distinguished from phenyl overtones. Assignments should be possible after preparation of a deuterated sample. [g] ~5% solution in CD_3CN. [h] ν(Re–Cl). [i] ~10% solution in CD_2Cl_2. [j] No $\nu(C{=}C)$ observed, but 1500-cm^{-1} region is partly obscured by phosphine ligand absorption. [k] Obscured by ν(CO). [l] ν(CO). [m] ~5% solution in C_6D_6.

been reported for the analogous chloro complex, *trans*-$ReCl(N_2)(dppe)_2$, studied by Chatt and coworkers.[1,2]

Reaction of $(Et_4N)_2ReH_9$[3,4] with 1,2-bis(diphenylphosphino)ethane in 2-propanol solution[5] under a nitrogen atmosphere at 25° gives a yellow crystalline precipitate; the latter is a mixture of *trans*-$ReH(N_2)(dppe)_2$ (I) and, to a lesser extent, the known trihydride $ReH_3(dppe)_2$[6] (II). Recrystallization of the crude product from benzene affords pure I.[7] Under an argon atmosphere or at reflux temperature under a nitrogen atmosphere no dinitrogen complex is formed. The reactions of monotertiary phosphines with $(Et_4N)_2ReH_9$ in a nitrogen atmosphere lead only to hydride complexes[8] with no evidence of the formation of an N_2 complex.

$ReH(N_2)(dppe)_2$ is a moderately air-stable compound; Table I summarizes some significant spectroscopic properties. The presence of a coordinated N_2 group in I is demonstrated by the very strong ir absorption at 2006 cm^{-1}, assigned as $\nu(N\equiv N)$; a weak band at 1818 cm^{-1} is assigned as ν(Re–H). The quintet of relative intensity 1 (relative intensity of dppe methylene protons = 8) at τ 19.94 in the ^1H nmr spectrum confirms that a single metal-bonded hydrogen is present. The latter is coupled equivalently to the four phosphorus atoms, and, since the nmr spectrum shows no significant temperature dependence down to ~ −110°, we conclude that the phosphorus atoms are in fact geometrically equivalent. I must therefore have trans-octahedral geometry. The observed phosphorus–hydrogen coupling constant is consistent with this since it is in the range expected for H cis to P.[9] A crystal structure determination[10] on the related complex $ReCl(N_2)(PMe_2Ph)_4$[1] has shown it to have the trans configuration.

trans-$ReH(N_2)(dppe)_2$ is readily protonated at the metal to form a seven-coordinated dihydridodinitrogenrhenium(III) cation. The complex precipitates as the cream colored tetrafluoroborate salt, $[ReH_2(N_2)(dppe)_2]BF_4$[7a] (III), on treatment of a benzene solution of I with a stoichiometric amount of HBF_4. Formulation of III as a 1:1 electrolyte has been confirmed by conductivity measurements in acetonitrile solution over the concentration range 10^{-2}–10^{-3} *N* (Λ_0, 136; *A*, 289 (calcd, 330)). Pertinent spectroscopic data are given in Table I.

Protonation of I with HCl gave an as yet incompletely characterized mixture containing $[ReH_2(N_2)(dppe)_2]Cl$. Warming the mixture in benzene converts it to a monohydridodichloro complex, $ReHCl_2(dppe)_2 \cdot C_6H_6$[7] (IV). Complex IV is of interest because its high-field proton resonance (Table I) appears as a "triplet of triplets"; it is evidently not fluxional and contains two nonequivalent pairs of phosphorus atoms. In contrast to IV, none of the other known seven-coordinate bis(dppe)–rhenium hydride complexes show evidence of nonequivalent phosphorus atoms in their nmr spectra.[11]

Metal hydrides react with halocarbons to form halide complexes. Under appropriate conditions I undergoes such reactions without disrupting the Re–N_2 bond. Thus, when a benzene solution of I is allowed to react with methyl iodide, an orange-yellow iododinitrogen complex, $ReI(N_2)(dppe)_2$[7] (V), is formed. The yellow bromodinitrogen complex VI[7a] is obtained by a similar reaction with CH_3Br. VI has been obtained previously in impure form by another route,[1] but V is a new compound. The known chlorodinitrogen complex could not be prepared by reaction of I with CH_3Cl. Examination of the phenyl region ^1H nmr spectra of V and VI (in CS_2 and CD_2Cl_2 solutions) shows no evidence of an ortho phenyl–hydrogen triplet upfield from the phenyl multiplet. Since such triplets are characteristic of *cis*-$M(dppe)_2XY$ complexes,[12] we assume that V and VI, like I, have trans-octahedral geometry.

Oxidative addition reactions are common with d^8 and d^{10} group VIII metal complexes,[13] but are very rare with complexes of non-group VIII metals. An

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example is provided by the reaction of H_2 with I, a six-coordinate Re^{I} complex, to form the seven-coordinate Re^{III} complex II. This reaction is not reversed under 60 psi of N_2 pressure; in this respect it is unlike the addition of H_2 to $CoH(N_2)L_3$ to form CoH_3L_3, a readily reversible reaction.

A hydrido–ethylene complex, $ReH(C_2H_4)(dppe)_2$[7] (VII), is formed on shaking a benzene solution of I under 60 psi of ethylene pressure. No evidence was found for insertion of C_2H_4 into the Re–H bond; retention of the latter in VII is demonstrated by the τ 16.92 quintet in the ^1H nmr spectrum. The bound ethylene proton resonance occurs at τ 7.64 (CS_2 solution),[14] considerably shifted from the value for free ethylene (τ 4.67 in CCl_4) or ethylene in Zeise's salt (τ 5.27),[15] but not excessively different from the shift for π-bonded ethylene (ν(C=C), 1541 cm^{-1}) in $[Re(CO)_4(C_2H_4)_2]PF_6$ (τ 6.6 in D_2O).[16] It appears reasonable to formulate VII as a six-coordinate π-ethylene complex of Re^{I}, and to view its formation as a simple substitution reaction. The only other stable hydrido–ethylene complexes of which we are aware are $NbH(C_5H_5)_2(C_2H_4)$[17a] and *trans*-$[PtH(C_2H_4)(PEt_3)_2]BPh_4$;[17b] the latter has been formulated as a four-coordinate π-ethylene complex.

Carbon monoxide slowly displaces N_2 from I in benzene solution to form the carbonyl analog, *trans*-$ReH(CO)(dppe)_2$[7] (VIII), in quantitative yield. That VIII has retained trans geometry is confirmed by the presence of a high field quintet and its value of J(P–H) (Table I). The low value of ν(CO) is consistent with the suggestion of Chatt, *et al.*,[1] that terminal carbonyl complexes with low ν(CO) will have dinitrogen analogs. Finally, we note that the higher value of τ(Re–H) for the N_2 complex I, as compared to the CO complex VIII, suggests that N_2 has a somewhat smaller trans influence than CO.[9] A similar conclusion has been reached on other grounds.[18]

Acknowledgment. We thank Mr. C. R. Sprinkle for the preparation of starting materials and the molecular weight determinations.

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Steric Hindrance in Triplet Electronic Energy Transfer[1]

Sir:

Systematic studies of the rates of triplet electronic energy transfer processes have mainly focused upon the effects of energetics on the efficiency of energy transfer.[2–4] These studies have led to the following conclusions: (1) when the triplet energy of the donor exceeds the triplet energy of the acceptor by more than 3 kcal/mol, the energy transfer rate is at the diffusion-controlled limit; (2) as the triplet energy of the donor decreases below this level, energy transfer rates drop very sharply. Several exceptions to these general rules have been noted and explained as steric hindrance to triplet energy transfer.[5–8] Since the accepted electron-exchange formulation for triplet energy transfer requires an effective collision between the donor and acceptor molecules,[9] the possibility of steric hindrance might be expected. However, there have been no systematic studies of the magnitude of steric effects upon the rates of triplet electronic energy transfer.[10]

We have measured the rates of quenching of triplet triphenylene in benzene solution by a series of azo compounds with a variety of steric properties. The triplet energy of triphenylene has been established to be 66.6 kcal/mol in a nonpolar solvent.[11] The determination of triplet energies for aliphatic acyclic azo compounds has been more difficult, but the best estimates are about 53–56 kcal/mol.[12,13] Thus, triplet energy transfer from triphenylene to an azo compound is sufficiently exothermic to allow a prediction of a diffusion-controlled rate constant. Small substituent effects upon the triplet energies of individual azo compounds should not affect this prediction. We have found, however, that the rate of triplet energy transfer from triphenylene to azo compounds can be substantially less than the diffusion-controlled limit, depending upon the steric bulk of the substituents surrounding the azo functional group.

All of the azo compounds were synthesized by the method of Stowell[14] and were determined to be >95% pure by gas chromatographic analysis. Samples were prepared in purified[4] benzene and degassed by five freeze–pump–thaw cycles to an ultimate pressure of at least 10^{-5} Torr. Quenching rates were determined by standard flash photolytic kinetic techniques,[4] using a modified Xenon Model 710 apparatus.[15] Rate constants were obtained as the slopes of linear Stern–Volmer plots of observed first-order decay rate constants,

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