**Table I.** Solvolytic Rate Constants for 2-(Trifluoromethyl)-2-adamantyl Tosylate (**1**) at 25 °C

| solvent[a] | $Y_{OTs}$ | $k_{obsd}$,[b] $s^{-1}$ | $k_{rel}$-(2-AdOTs/**1**)[d] |
|---|---|---|---|
| $CF_3CO_2H$ | 4.57 | $4.97 \times 10^{-4}$ | 1.81 |
| 97% $(CF_3)_2CHOH$ | 3.61 | $3.43 \times 10^{-5}$ | 2.84 |
| $HCO_2H$ | 3.04 | $1.39 \times 10^{-5}$ | 1.91 |
| 97% $CF_3CH_2OH$ | 1.83 | $1.20 \times 10^{-6}$[c] | 1.37 |

[a] TFA, HFIP, and TFE are $CF_3CO_2H$, $(CF_3)_2CHOH$, and $CF_3CH_2OH$, respectively. [b] Measured by UV spectroscopy; at least two determinations of each rate constant. [c] Extrapolated from the following: $2.71 \times 10^{-4}$ $s^{-1}$ (73.4 °C), $2.83 \times 10^{-5}$ $s^{-1}$ (52.1 °C), and $1.42 \times 10^{-5}$ (45.3 °C); $\Delta H^* = 22.5$ kcal/mol, $\Delta S^* = -10.2$ eu. [d] 2-AdOTs values from ref 6a.

We attribute the remarkably high reactivity of **1** to a combination of relief of ground-state strain[3c,7] and electron donation from the $C_3$–$C_4$ bond. Even though $CF_3$ is often thought of as a small group, it is significantly larger than $CH_3$ by a variety of measures,[8] and steric effects of substituents are proposed[3c] to be enhanced in rigid adamantyl as opposed to more flexible systems. Calculations using the program Macromodel 2 indicate a 4.0 kcal/mol greater energy for the $CF_3$ in **1** compared to the axial $CF_3$ in *trans*-4-*tert*-butyl-1-(trifluoromethyl)cyclohexyl tosylate, so the *A* value of 2.5 kcal/mol for $CF_3$[8a] leads to a crude estimate of 6.5 kcal/mol for the total strain due to $CF_3$ in **1**. Solvolysis transition states resemble fully formed carbocations,[9a] so essentially all this strain can be lost in the transition state, causing an acceleration in the rate of **1**.

There is strong recent evidence for electron donation from the $C_3$–$C_4$ bond in adamantyl cations,[9b–f] and such participation in **1** leads to the cation **2**, which forms the protoadamantyl ring system **3** (eq 1). The protoadamantyl system is estimated to be 11 kcal/mol more strained than the parent adamantyl system,[3d] but substituents at the 3-position in protoadamantane as in **3** are not crowded.[3d] Thus formation of the transition state leading to **2** results in a decrease in the $CF_3$ nonbonding interaction of **1** but an increase in ring strain characteristic of **3**. A strong electronic driving force for formation of an ion which diminishes positive charge buildup adjacent to $CF_3$ is expected.[10] Rearrangement[11a] without appreciable kinetic acceleration[11b,c] occurs in related acyclic systems.

2-Benzoyl-2-adamantyl mesylate (**6**) is more reactive than 2-adamantyl mesylate by factors ranging from 164 to 356,[6c,d] and while steric effects were considered to account for this high reactivity, conjugative effects were favored. Similarly 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate was proposed to "solvolyse without significant steric acceleration".[12] This may be true, but our results suggest that steric effects in formation of 2-adamantyl carbocations should not be underestimated.

The molecular structure of **1** determined by X-ray by Dr. Jeffery Sawyer requires further refinement but shows geometrical distortions due to strain, including bending of the $CF_3$ group away from the adjacent axial hydrogens which still have close contacts (2.27 and 2.36 Å) with one of the fluorines. Our own studies of the correlation of chemical reactivity with X-ray structure[13a,b] make us more cautious than others[13c] in cause and effect interpretations of such results, but the structural distortions are at least consistent with major steric interactions, as also seen in 2-cumyl-2-adamantanol.[13d]

In summary, the destabilizing effect of the $CF_3$ group in the solvolysis of **1** is drastically attenuated, a result attributed to relief of ground-state strain and electron donation from the $C_3$–$C_4$ bond. This result has implications for the consideration of the size of fluorinated groups and for possible effects of steric strain in other adamantyl systems, such as 2-benzoyl-[6c,d] and 2-(trimethylsilyl)adamantyl sulfonates,[12] in which possible steric effects were discounted.

**Acknowledgment**. The financial support of the Natural Sciences and Engineering Research Council of Canada, NATO, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. National Science Foundation and helpful discussions with Professor G. A. Olah are gratefully acknowledged. The Macromodel 2 calculations were carried out by Dr. R. C. Kelly using facilities kindly provided by Professor P. A. Wender at Stanford University.

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# Regiocontrolled and Stereocontrolled C–C Bond Formation via Linear Dimerization of Conjugated Dienes Catalyzed by Nickel–Aminophosphinite Complexes

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Linear dimerization of butadiene $2C_4H_6 \rightarrow$ 1,3,6-octatrienes has been shown to occur readily at room temperature on nickel catalysts modified by aminophosphinite ligands $Ph_2POCHR^1CHR^2NHR^3$ (AMP).[1] With such complexes, obtained by interaction between $Ni(COD)_2$ and these AMP ligands, the reaction rate is ca. 1–2 orders of magnitude higher than observed in other systems using either morpholine,[2] ethanol,[3] or *P*-methyloxaphospholidines[4] as modifiers. The higher reactivity of these new Ni–AMP systems prompted us to study the mechanism of the reaction upon using labeled reagents and the extension of this catalysis to other substituted and functionalized 1,3-dienes.

In order to prove the contribution of the pendant NH moiety in the reaction pathway, we have first conducted the reaction with perdeuterated butadiene $C_4D_6$ to obtain almost pure deuterated 1,3,6-octatrienes.[5] A second experiment involved the use of a

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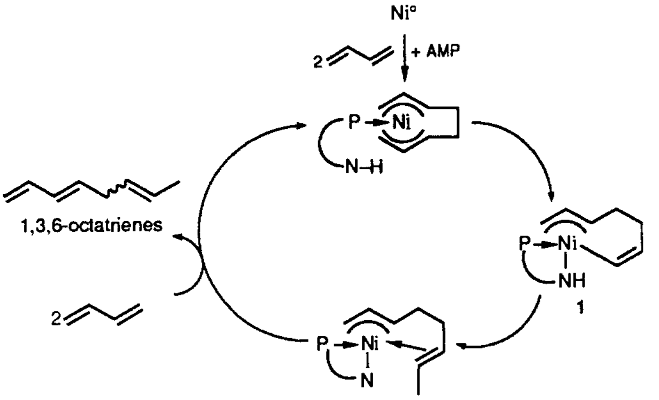
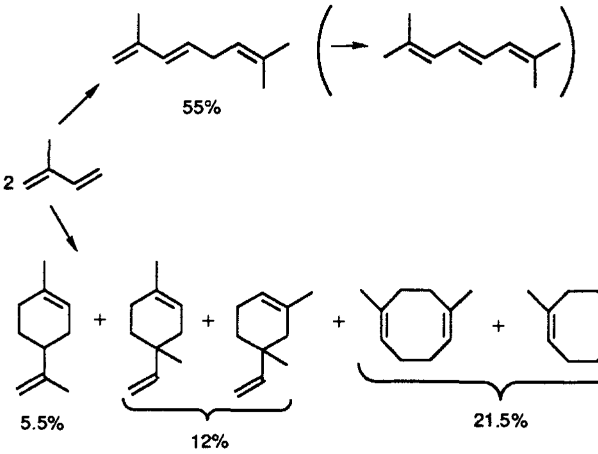
(5) The experimental conditions are typically those used in our preliminary work (see ref 1), with the (D)EPHOSNH [$Ph_2POCH(Ph)CH(Me)NHMe$] ligand.

0002-7863/90/1512-1292$02.50/0

**Scheme I**



**Scheme II**



deuterated $PPh_2OCH(Ph)CH(Me)NDMe$ [(D)EPHOSND] ligand, with $C_4H_6$ as substrate: the reaction was then stopped rapidly in order to analyze the dimer products arising from the first turnover of the catalytic reaction.[6] From a comparison between the deuterium spectra of perdeuterated octatrienes and that of this compound, we have been able to assign unambiguously the presence of deuterium at the C-8 carbon atom of the triene, that is, $CH_2{=}CHCH{=}CHCH_2CH{=}CHCH_2D$.[7] This is in total agreement with a previous mechanistic hypothesis by Heimbach,[2] where the NH moieties of morpholine were suggested to be responsible for the production of linear dimers, via oxidative addition on an ($\eta^1{:}\eta^3$-octadienediyl) complex **1** followed by hydrogen addition on the $\sigma$ part of the C-8 complexed ring, and $\beta$ hydrogen elimination at C-4 to give the 1,3,6-octatriene derivatives (Scheme I).

Attempts to dimerize isoprene and piperylene were done on the same catalytic system. In the case of isoprene, both cyclic and linear dimerization occurred, although the linear compounds predominate (Scheme II). The catalytic activity decreases greatly, however, as compared to butadiene; for a substrate/catalyst ratio of 50, a 90% conversion was only obtained after 19 h at 40 °C [AMP = (D)EPHOSNH].

An interesting feature to be considered here is the fact that only a *tail to tail* linkage is observed to produce initially a mixture of 2,7-dimethyl-1,3,6-octatrienes which isomerize further into the 2,4,6 conjugated isomers.

The behaviour of 1,3-pentadiene is very interesting in several respects (Scheme III): (i) A 95% conversion is obtained at 40 °C within 3 h for a substrate/Ni ratio of 100. (ii) The reaction gives exclusively linear dimers. (iii) These arise from a selective *head to head* linkage, and therefore, the reaction produces prochiral 4,5-dimethyl-1,3,6-octatrienes. An isomerization process occurs also as a consecutive reaction. (iv) As soon as a chiral ligand is used [(1*R*,2*S*)-EPHOSNH], the catalytic mixtures are optically active. Isolation of the *E,E* and *E,Z* isomers of 4,5-dimethyl-1,3,6-octatriene gives pure products whose specific rotation $[\alpha]^{20}_D$ are +26° and −143°, respectively.

**Scheme III**

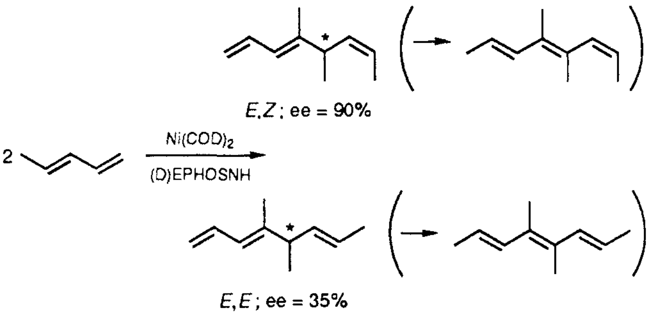
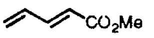
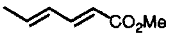


Table I. Linear Dimerization of Dienic Esters on $Ni(COD)_2$–(D)EPHOSNH Catalysts

| diene | diene/ Ni | *T*, °C | time, h | convn, % | product |
|---|---|---|---|---|---|
|  | 50 | 40 | 0.5 | 98 | $MeO_2CCH{=}CHCH{=}CHCH_2CH{=}CHCH_2CO_2Me$ (seven isomers) |
|  | 50 | 80 | 46 | 92 | $MeO_2CCH{=}CHCH{=}C(Me)\text{-}CH(Me)CH{=}CHCH_2CO_2Me$ (85% *E,E,E*, 13% *E,E,Z*) |

The separation of the enantiomers was performed via the LIS technique, upon using a mixture of $Eu(tfc)_3$ and Ag(fod) (tfc = trifluoroacetylcamphorato; fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctanedione). Provided the Ag(fod) was added to the olefinic compound, a splitting occurs at the vinylic proton on C-6. This allowed estimation of the ee's of the *E,E* and *E,Z* isomers as 35 ± 5 and 90 ± 5%, respectively.

Concerning functionalized diene dimerization on nickel catalysts, the results obtained so far in the literature have shown that only esters and silyl ethers could be transformed into cyclodimers, using a low substrate/catalyst ratio and long reaction times (1 day).[8,9]

With this new system, linear dimerization is observed with dienic esters, whereas it fails with other functionalized groups such as $NEt_3$, OMe, $OSiMe_3$, and OAc.

Good activity is observed with methyl penta-2,4-dienoate, with an exclusive *tail to tail* linkage into linear dimers (Table I).

Although the reaction requires higher temperatures and reaction times with methyl sorbate, the new dimers 1,8-bis(methoxycarbonyl)-4,5-dimethyl-1,3,6-octatriene are produced as an *E,E,E* and *E,E,Z* mixture and gave specific rotations of −2° and −1.5°, respectively. This shows again that the dimerization occurs regioselectively, and also with some enantioselectivity, for which analyses are in progress to determine the ee's.

Further studies will be carried out in due course in order to apply this catalytic system to cross reactions between different dienes for generalization of this process.

**Supplementary Material Available:** General procedures for syntheses of the aminophosphinite ligands and catalytic reactions,

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[6] This experiment used *n*-pentane as solvent and a butadiene/nickel ratio of 5, at 0 °C, the reaction being stopped rapidly in order to avoid further production of unlabeled octatrienes.

[7] The NMR signal of this allylic deuterium atom is easily distinguished from the resonances of the other deuterium atoms, the nearest neighboring signals (allylic $CD_2$) appearing at 1.1 ppm downfield.

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infrared and $^1H$ and $^{13}C$ NMR data for dimers described in this work, $^2H$ NMR spectra of perdeuterated and monodeuterated octatrienes, and 400-MHz $^1H$ NMR spectra of (*E*,*E*)-4,5-dimethyl-1,3,6-octatriene without and in the presence of Eu(tfc)$_3$ and Ag(fod) (5 pages). Ordering information is given on any current masthead page.

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# Dihydrogen Complexes of Metalloporphyrins: Characterization and Hydrogen-Transfer Reactivity

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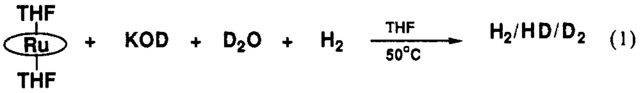
Extensive reports of $\eta^2$ coordination of dihydrogen to transition metals[2] have recently led to speculation that the $\eta^2$-dihydrogen complexes and their corresponding transition-metal hydrides may be important in the biological activation of molecular hydrogen.[3] We now report that protonation of transition-metal porphyrin hydrides has yielded the first known dihydrogen complex of a metalloporphyrin and a system that performs some functions of hydrogenase enzymes.[4]

The previously reported monohydrides,[5,6] K[M(OEP)(H)], M = Ru (**RuH**), Os (**OsH**), were prepared by potassium metal reduction of the corresponding dimers [M(OEP)]$_2$ in THF followed by protonation with excess water or *tert*-butyl chloride. The $^1H$ NMR spectrum shows that protonation of **OsH** with benzoic acid in THF affords in approximately 30% yield a porphyrinic product formulated as Os(OEP)(H$_2$), **OsH**$_2$.[7,8] In particular, the high-field singlet of **OsH**$_2$ ($\delta$ -30.00)[9] is replaced by a triplet ($\delta$ -30.01, $^1J_{HD}$ = 12 Hz) when Os(OEP)(HD), **OsHD**, is formed by the reaction of **OsH** with benzoic acid-$d_1$. The magnitude of this coupling and the minimum observed relaxation time ($T_1$ = 110 ± 8 ms for **OsH**$_2$ at -20 °C in THF) suggest the presence of an $\eta^2$-dihydrogen ligand.[10,12] In addition, the methylene protons of the OEP ethyl substituents appear as a multiplet in the 400-MHz NMR spectrum, indicating that the two faces of the porphyrin are inequivalent[17] and precluding the presence of the *trans*-dihydride.

The above NMR parameters are consistent with formulation of **OsH**$_2$ as a dihydrogen complex rather than a *cis*- or *trans*-dihydride. However, both $^1J_{HD}$ and $T_1$ are near the limits proposed for formulation as $\eta^2$ coordination. The 12-Hz coupling constant is notably lower than that seen for most molecular hydrogen complexes in the literature (18 Hz < $^1J_{HD}$ < 34 Hz),[2] although values as low as 13.7 Hz have been reported.[18] Additionally, $T_1$ is in the upper limit of the range acceptable for unambiguous classification as a molecular hydrogen complex. Together, these parameters suggest a weaker H-H interaction than found in most dihydrogen complexes. Because the H$_2$ binding mode is suggested to be dependent upon backbonding from the metal, dinitrogen stretching frequencies of L$_n$M(N$_2$) complexes (diagnostic of the extent of metal backbonding to the N$_2$ ligand) have been used to predict the stability and coordination mode of the corresponding L$_n$MH$_2$ complexes.[19] The $\nu$(N$_2$) for Os(OEP)(THF)(N$_2$) is 2030 cm$^{-1}$,[20] which is in the range where the corresponding H$_2$ complex, **OsH**$_2$, is expected to exist as a dihydride (<2060 cm$^{-1}$), and slightly below the range used to predict stable $\eta^2$-H$_2$ complexes (2060-2150 cm$^{-1}$). Such a $\nu$(N$_2$) value reflects strong backbonding by the Os(II) center, a property conducive to increasing the dihydride character of the dihydrogen complex. The $T_1$, $^1J_{HD}$, and $\nu$(N$_2$) values are thus self-consistent and suggest that the electronic nature of Os(OEP) favors dihydride formation but that the rigid porphyrin constrains the H$_2$ to a single coordination site.

Since the dinitrogen stretching frequency for Ru(OEP)(THF)(N$_2$) is 2110 cm$^{-1}$,[21] a dihydrogen complex of Ru(OEP) should have less dihydride character than the osmium analogue. Protonation of **RuH** with benzoic acid in THF results in rapid quantitative loss of dihydrogen to yield the bis solvato complex, Ru(OEP)(THF)$_2$, **Ru(THF)**$_2$. Such hydrogen loss is not surprising since Ru(II) is substitutionally more labile than Os(II). Even under 1 atm of H$_2$ in THF, **Ru(THF)**$_2$, known to be substitutionally labile,[22] does not form the proposed Ru(OEP)(H$_2$) in quantities observable by $^1H$ NMR.

Although we have been unable to observe Ru(OEP)(H$_2$) by NMR, its presence is suggested by the catalytic activity of **Ru(THF)**$_2$ for H/D isotope exchange. A 10 mM solution of **Ru(THF)**$_2$ in THF containing 12 equiv of KOD and 570 equiv of D$_2$O exchanges 6.9 equiv of deuterium between D$_2$O and H$_2$ gas when stirred at 50 °C under 0.13 atm of H$_2$ for 160 min[23] (eq 1). In



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[6] Abbreviations: OEP = octaethylporphyrinato dianion; THF = tetrahydrofuran; NAD$^+$ = nicotinamide adenine dinucleotide (oxidized form).

[7] Os(OEP)(H$_2$): NMR (THF-$d_8$, 400 MHz) H$_{meso}$ 9.29 (s), CH$_2$ 3.83 (m), CH$_3$ 1.81 (t), Os(H$_2$) -30.00 (s) ppm.

[8] The axial ligation of this species is unclear, though THF-$d_8$ is suspected.

[9] Transition-metal hydride resonances of porphyrins are shifted to very high field by the porphyrin ring current effect.[5] The hydride resonance of **OsH** before protonation to **OsH**$_2$ is -65.6 ppm.

[10] $^1J_{HD}$ for *cis*-dihydrides are typically <1 Hz,[11] 1 order of magnitude smaller than those typical of dihydrogen complexes.

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[12] Relaxation times were measured over the temperature range -80 to 20 °C. This minimum $T_1$ value is within the range generally accepted for classification of the complex as a molecular hydrogen complex (<160 ms at 400 MHz).[13-16]

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