to a volume of 2 L with distilled water, and the pH was adjusted to 7.2. Magnesium chloride (50 mmol) and 1,3-dimercapto-2-propanol (20 mmol, protein antioxidant)[17] were added, and the reaction was blanketed with argon. Diammonium acetyl phosphate solution[18] (AcP, 1 M, pH 7.0, stored at 0 °C) was added with stirring by peristaltic pump to maintain an ATP concentration above K_m for NADPP (0.5 mM). Additional NMN (20 mmol) and AMP (25 mmol) were added over 10 days. At the conclusion of the reaction, 100 mmol of AcP had been added and 39 mmol of NAD produced (97% based on NMN). The enzyme-containing gel was allowed to settle, and the reaction mixture was decanted. A repetition of the reaction on the same scale and using the same enzymes consumed 110 mmol of AcP and generated 37 mmol of NAD (91% based on NMN).

The solutions containing NAD could be used directly, without further purification, to provide NAD (or NADH) for cofactor-requiring enzymatic synthesis.[19] Treatment of this crude NAD-containing solution with NAD kinase (EC 2.7.1.23) and ATP (using the ATP regeneration system) also generated NADP uneventfully. Thus, whatever the impurities present in the unpurified NAD may be, they do not appear to inhibit or inactivate other enzymes. If desired, however, solid NAD can be obtained in >50% purity by acidifying the solution with Dowex 50 (H^+ form), precipitating impurities with $Ba(OH)_2$, and precipitating NAD^+ with ethanol.

This work has several interesting features. First, this synthesis of NAD from readily available starting materials involves only one isolation (of r-5-P; this isolation is required only to dry the r-5-P and is straightforward). For all other steps, unpurified reaction mixtures are used directly, and enzymatic selectivity is used to direct reactants efficiently to products. Isolations and separations of nucleotides are laborious: a synthesis which requires only one simple separation has an advantage in convenience. Second, the NAD produced appears to be suitable for use in cofactor recycling procedures *without further purification*. Thus, although the NAD produced here is only ~15-20% pure (without purification), its simple synthesis and its demonstrated utility in cofactor recycling should make it useful in enzyme-catalyzed organic synthesis. Third, all of the enzymes required for the synthesis are easily immobilized and very stable: the manipulation of the enzymatic catalysts is thus straightforward. Finally, we note that the facile synthesis of rA-5-P should find application in other areas of nucleotide chemistry, that the use of r-5-P as starting material avoids many of the problems encountered in more extensively developed synthetic routes to nucleotides, by avoiding the protecting groups often required to generate a product having the furanose configuration, and that preliminary studies suggest that NADPP has sufficiently broad specificity to catalyze the coupling of NMN and ATP moieties bearing at least some structural modifications.

(17) Szajewski, R. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 2011-2026.

(18) Lewis, J. M.; Haynie, S. L.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 864-865.

(19) For example, a turnover number of 1000 was obtained for NAD(H) in the preparation of D-lactate from pyruvate. The reaction mixture (20 mL) contained 0.05 mM NAD (0.34 mL of the solution prepared as described), glucose 6-phosphate (50 m*M*), pyruvate (50 m*M*), glucose-6-phosphate dehydrogenase (50 U) and D-lactate dehydrogenase (50 U). Reaction was complete in 24 h and generated D-lactate quantitatively. Indistinguishable results were obtained by using pure NAD (Sigma). Similar results have been obtained with lipoamide dehydrogenase and horse liver alcohol dehydrogenase. Impurities also do not seem to inhibit the enzymes used to make and assay NAD and NADP.

(20) CONACYT-MEXICO Predoctoral Fellow.

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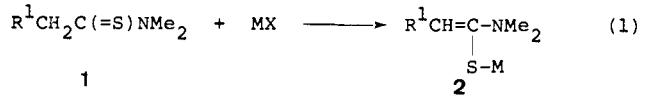
Stereoselective Generation of *Z*-Enolates of Thioamides: Its Application to Diastereoselective Aldol Condensations and Thio-Claisen Rearrangements

Sir:

Compared with ordinary carbonyl compounds (ketones, esters, amides, etc.) and thiocarbonyl compounds (dithioesters,[1] thioketones,[2] etc.), thioamides are exceptionally reluctant to undergo carbophilic[3] or thiophilic addition of organometallics. This characteristic behavior in conjunction with our work on Michael addition reactions of a wide range of organometallics to α,β-unsaturated thioamides[4] suggests that thioamides are most likely to undergo proton abstraction α to the thiocarbonyl group to generate thioenolates in the reaction with organometallics.[5] Indeed, this proved to be the case and the enolates with Na^+ (**2b,c**) Li^+ (**2a-c**), and Mg^{2+} (**2a-c**) gegenions were generated very conveniently simply by exposure of thioamides to NaH (THF-Me_2SO, room temperature), *n*-BuLi (THF, -78 °C), and *i*-PrMgBr (THF, room temperature or 65 °C), respectively (eq 1).

Here we report diastereoselective aldol condensations and thio-Claisen rearrangements which take advantage of the ready availability of the thioamide enolates **2** in high geometrical purity (vide infra).

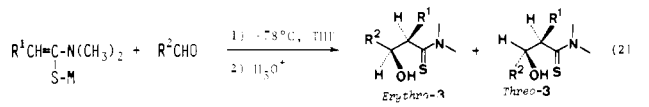


(1)

1 **2**

a, $R^1 = CH_3$
b, $R^1 = Ph$
c, $R^1 = SPh$

Mx = *n*-BuLi, *i*-PrMgBr, or NaH



(2)

It is well documented that the appearance of kinetic aldol selection is attributed to the six-membered chairlike transition state with the R^2 group of the aldehyde in an equatorial position (Scheme I).[6] On this ground, the *E*-enolates of thioamides, as suggested by Brandsma et al.,[7] are expected to give rise to the *threo*-β-hydroxythioamides (*threo*-**3**) selectively. However, as

(1) (a) Meyers, A. I.; Tait, T. A.; Comins, D. L. *Tetrahedron Lett.* **1978**, 4657. (b) Burgot, J.-L.; Masson, J.; Vialle, J. *Ibid.* **1976**, 4775. (c) Gosselin, P.; Masson, S.; Thuillier, A. *J. Org. Chem.* **1979**, *44*, 2807.

(2) (a) Dagnonneau, M.; Vialle, J. *Tetrahedron* **1974**, *30*, 415. (b) Metzner, P.; Vialle, J.; Viet, A. *Tetrahedron Lett.* **1976**, 4295. (c) Burgot, J.-L.; Masson, J.; Metzner, P.; Vialle, J.; *Ibid.* **1976**, 4297. (d) Gassman, P. G.; Mullins, M. J. *Ibid.* **1979**, 4457; **1980**, *21*, 2219.

(3) (a) Beak, P.; Yamamoto, J.; Upton, C. J. *J. Org. Chem.* **1975**, *40*, 3052. (b) Walter, W.; Lüke, H.-W. *Angew. Chem.* **1977**, *89*, 550.

(4) (a) Tamaru, Y.; Harada, T.; Iwamoto, H.; Yoshida, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5221. (b) Tamaru, Y.; Harada, T.; Yoshida, Z. *Ibid.* **1979**, *101*, 1316.

(5) For the metalation of the *N*-CH_3 of *N,N*-dimethylthiopivalamide with *sec*-BuLi, see: Seebach, D.; Lubosch, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 313.

(6) (a) Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979**, *101*, 6120. For diastereoselective aldol condensations of ketone enolates, see: (b) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *Ibid.* **1973**, *95*, 3310. (c) Klebshick, W. A.; Buse, C. T.; Heathcock, C. H. *Ibid.* **1977**, *99*, 247. (d) Buse, C. T.; Heathcock, C. H. *Ibid.* **1977**, *99*, 8109. (e) Heathcock, C. H.; White, C. T. *Ibid.* **1979**, *101*, 7076. (f) Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, S. D.; Sohn, J. E. *Ibid.* **1979**, *101*, 7077.

(7) *E*-Ketene *S,N*-acetals were obtained selectively by Shuijl et al. (Shuijl, P. J. W.; Bos, H. J. T.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 1263) by the alkylation of enolates generated by treatment of thioamides with $NaNH_2$ in liquid NH_3. The geometry of the ketene *S,N*-acetals was determined on the basis of the ^1H NMR chemical shifts of the vinyl protons. Similar selectivity was also observed by us when we prepared ketene *S,N*-acetals by alkylation of enolates generated by treatment of thioamides with *sec*-BuLi in THF: Tamaru, Y.; Harada, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1978**, *100*, 1923.

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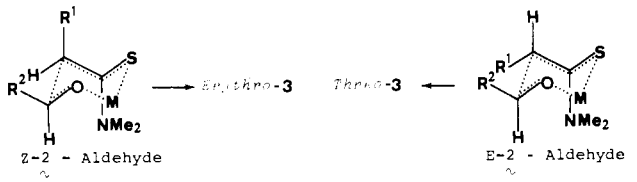
Table I. Diastereoselective Aldol Condensation Reactions

entry	R^1 of thioamides 1	aldehyde	metal	temp (°C)/ time (min)[a]	*erythro*-3:*threo*-3 ratio[b,c]
1	CH_3	$(CH_3)_2CHCHO$	Mg	−78/30	95:5
2	CH_3	C_6H_5CHO	Mg	−78/2	93:7
3	CH_3	C_6H_5CHO	Li	−78/2	87:13
4	CH_3	CH_3CH_2CHO	Li	−78/10	90:10
5	CH_3	CH_2=CHCHO	Mg	−78/30	89:11
6	C_6H_5	$(CH_3)_2CHCHO$	Mg	−78/2	72:28
7	C_6H_5	$(CH_3)_2CHCHO$	Mg	room temp/60	3:97
8	C_6H_5	CH_2=CH(CH_3)CHO	Mg	−78/10	73:27
9	C_6H_5S	$(CH_3)_2CHCHO$	Mg	−78/15	66:34
10		$(CH_3)_2CHCHO$	Li	−78/10	19:81

[a] The temperatures and times are for the reactions of enolates with aldehydes. [b] The ratio was determined by high-pressure liquid chromatography (Waters Associates dual-pump flow gradient system, 1-ft μ-Porasil column, (75–85):(25–15) *n*-hexane–EtOAc eluent, flow rate 1.5 mL/min). [c] Combined isolated yields range from 85% to almost quantitative.

Scheme I



observed in Table I, all of the reactions of **2a** and **2b** were highly erythro selective (entries 1–6 and 8) and the selectivity was almost independent of the gegenions[8] and the conditions of enolate formation (for the Li^+ gegenion, at −78 °C with either *n*-BuLi or lithium diisopropylamide; for the Mg^{2+} gegenion with *i*-PrMgBr either at room temperature for 4 h or at 65 °C for 1 h). These results suggest that thioenolates **2a–c** possess a *Z* configuration, which is further supported by the reverse selectivity observed in the reaction with the enolate of *N*-methylthiopyrrolidone (entry 10).[9] Especially rewarding is that the aldol selectivity is independent of the procedure of enolate formation: the results in Table I are those obtained by the reactions of enolates generated by the addition of organometallics to THF solutions of thioamides. The same results as those in entries 4 and 6 in Table I were obtained with enolates **2a,b** generated by a slow addition of THF solutions of **1a,b** to the THF–hexane solutions of *n*-BuLi (1.2 equiv, at −78 °C). The generation of *Z*-enolates by the latter procedure (kinetic control)[10] is quite unusual[12] in light of the deprotonations of carbon acids, which are known to provide *E*-enolates by a kinetically controlled process.[14]

The selectivity of aldols with **2b** is quite dependent on the reaction temperature and time (entries 6 and 7). A similar temperature–time dependency, but to a lesser extent than for **2b**, was also observed for the reaction of **2a** with benzaldehyde (figures are given in the order temperature, time, erythro:threo ratio: −78 °C, 2 min, 93:7; room temperature, 1 h, 90:10; 40 °C, 1 h, 80:20; 40 °C, 28 h, 17:83).[15] The dramatic increase in thermodynamically controlled *threo*-**3** may be attributed to the strong coordination of the sulfur atom to the metal to form a six-membered cyclic intermediate.

The results presented here seem to represent the efficient erythro-selective aldols of carboxylic acids[16] and their derivatives (esters,[17] thiolesters).[6a,18] Interestingly, the corresponding amides did not exhibit any significant selectivity.[19] The stereochemistry

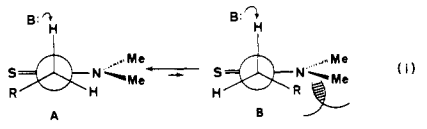
(8) While enolate **2c** (Mg^{2+} gegenion) reacted with aldehyde to provide aldol products (entry 9, Table I), **2c** (Na^+ gegenion, generated by NaH in THF at room temperature for 1 h) did not give any aldol products; instead **1c** was recovered completely. On the other hand, **2c** (Na^+ gegenion) provided the Michael addition products on reaction with crotonaldehyde (27% yield, a 1:1 diastereomeric mixture of *N,N*-dimethyl-2-(phenylthio)-5-oxo-3-methylthiopentanylamide). The enolate **2b** (Na^+ gegenion, generated by exposure to 1.1 equiv of NaH in 5:1 THF–Me_2SO, room temperature, 20 h) reacted with formaldehyde to provide *N,N,N',N'*-tetramethyl-2,4-diphenyldithioglutarylamide (93%, a 1:1 diastereomeric mixture).

(9) The experimental procedure is as follows: To a solution of **1b** (2 mmol) in 4 mL of anhydrous THF is added a THF solution of *i*-PrMgBr (3 mL, ca. 2.5 mmol) in one portion at ambient temperature, and the mixture is stirred for 4 h and then cooled to −78 °C. A THF solution of isobutyraldehyde (2.5 mmol) is added in one portion and stirred for 2 min. Addition of 3 mL of 1 N HCl [1:1 H_2O–THF (v/v)] and subsequent extractive workup with ether, followed by purification by column chromatography (silica gel, hexane–benzene–EtOAc gradient), provided *erythro*-**3** (R^1 = Ph, R^2 = $(CH_3)_2CH$) and *threo*-**3** (R^1 = Ph, R^2 = $(CH_3)_2CH$) in the yields of 68 and 26%, respectively (entry 6). After addition of aldehyde, the reaction temperature is allowed to rise to ambient temperature and stirring is continued for an additional 1 h, during which time a white precipitate appears. Similar workup and a single recrystallization from ether–*n*-hexane provided pure *threo*-**3** (R^1 = Ph, R^2 = $(CH_3)_2CH$) in 92% yield (entry 7). *erythro*-**3** (R^1 = Ph, R^2 = $(CH_3)_2CH$): oil; ^1H NMR (CCl_4) δ 0.87 (d, *J* = 7 Hz, 3 H), 1.01 (d, *J* = 7 Hz, 3 H), 1.55 (m, 1 H), 3.16 (s, 3 H), 3.38 (s, 3 H), 3.8–4.1 (m, 3 H), 7.26 (br s, 5 H); IR (neat film) 3340 (br s), 1510 (s), 1390 (s), 1265 (s), 780 (s), 705 (s) cm^{-1}. *threo*-**3** (R^1 = Ph, R^2 = $(CH_3)_2CH$): mp 102–102.5 °C (ether–*n*-hexane); ^1H NMR ($CDCl_3$) δ 0.95 (d, *J* = 6 Hz, 6 H), 1.25 (m, 1 H), 3.30 (s, 3 H), 3.47 (s, 3 H), 3.9 (br s, 1 H), 4.0 (d, *J* = 9 Hz, 1 H), 4.36 (br d, *J* = 9 Hz, 1 H), 7.45 (m, 5 H); IR (KBr disk) 3480 (br s), 1510 (s), 1385 (s), 1240 (s), 780 (s), 720 (s) cm^{-1}.

(10) The present procedure seems to ensure the true kinetically controlled deprotonation because of the use of an excess strong base (*n*-BuLi) and the diminished carbo- and thiophilic reactivity of thioamides toward organometallics[11] as noted in the introduction of the text.

(11) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959.

(12) The anomaly may be explained in terms of the partial double-bond character of the C–N bond of thioamides,[13] which favors conformer A over conformer B because the latter experiences a large steric repulsion between the R and *N*-CH_3 groups (eq i). Abstraction of the proton perpendicular to the sp^2 plane of thioamide would generate *Z* and *E* enolates from conformers A and B, respectively. A similar mechanism has also been proposed by D. A. Evans for the deprotonation of amides (private communication).



(i)

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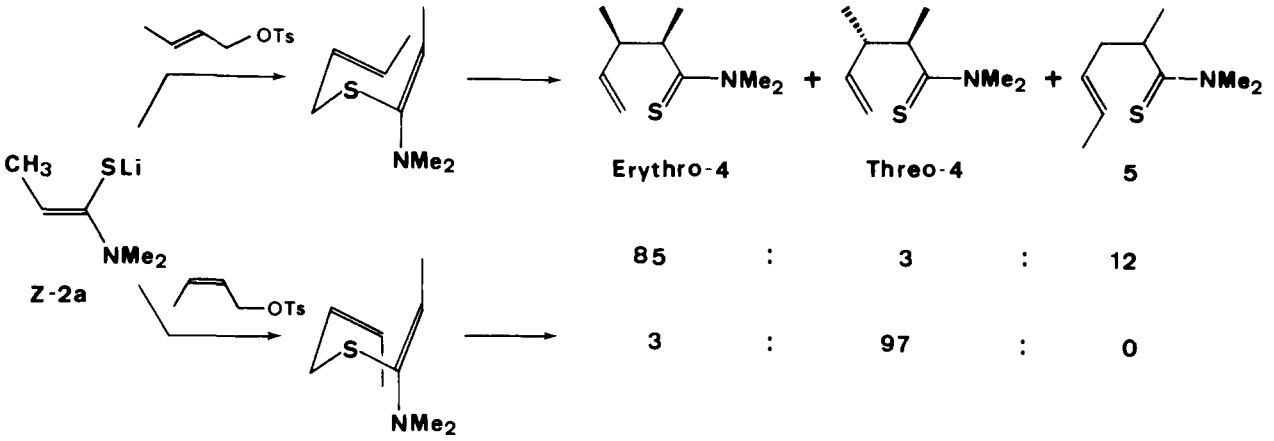
(15) The isolated yield was as high as 92% for the thermodynamic experiment.

(16) (a) Mulzer, J.; Segner, J.; Brüntrup, G. *Tetrahedron Lett.* **1977**, 4651. (b) Mulzer, J.; Brüntrup, G.; Fuike, J.; Zippol, M. *J. Am. Chem. Soc.* **1979**, *101*, 7723.

(17) (a) Meyers, A. I.; Reider, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 2501. (b) Pirrung, M. C.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1727.

(18) For the diastereoselective aldols of thiolesters via (vinyloxy)boranes, see: (a) Horn, D. E.; Masamune, S. *Tetrahedron Lett.* **1979**, 2229. (b) Hirama, M.; Garvey, D. S.; Lu, L. D.-L.; Masaume, S. *Ibid.* **1979**, 3937.

Scheme II



of the products was determined unequivocally by transforming each of the separated diastereomers to the corresponding esters, thiolesters, and/or carboxylic acids[20] and comparing the spectral data with those of authentic samples.[21] Just as with other aldols,[22] the carbinol resonances in the ^1H NMR spectra of β-hydroxythioamides appeared as J_{threo} (8–10 Hz) > $J_{erythro}$ (2–4 Hz).

The thio-Claisen rearrangements[23] seem to be ideal for obtaining further confirmation of the stereochemistry of the enolate and also for estimating the geometrical purity of the enolate because other methods, such as the ketene *S,N*-acetal technique,[7,24] might be plagued by thermal or catalytic isomerization and by the difficulty in the spectroscopic determination of trisubstituted olefins.

The enolate **2a** (Li^+ gegenion), on treatment with *cis*-crotyl tosylate at −78 °C (THF, 30 min), followed by refluxing for 2 h, provided a 3:97 ratio of *erythro*- and *threo*-*N,N*-dimethyl-2,3-dimethylthiopent-4-enamides (**4**) in 55% yield,[25] while the same reaction with *trans*-crotyl tosylate gave rise to an 85:3:12 ratio of *erythro*-**4**, *threo*-**4**, and a regioisomer **5** in 48% yield (Scheme II). These high stereoselectivities seem to be definite evidence for the *Z*-configuration of **2a** and its geometrical purity over 97%[26] because it is well-established that the Claisen rearrangements proceed preferentially through a chairlike transition state over a boatlike transition state.[27]

In conclusion, we have presented two methods which embody highly selective relative asymmetric induction, both of which might find wide applicability for the synthesis of macrolide antibiotics[28] and other natural products.

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(19) The reaction of the lithium enolate of *N,N*-dimethylpropionamide, generated by treatment with 1.1 equiv of LDA, with benzaldehyde provided an erythro–threo mixture in a ratio of 57:43. Similar results have been reported by Heathcock and co-workers.[6c]

(20) For example, *erythro*-*N,N*-dimethyl-3-hydroxy-2-methyldihydrothiocinnamide is converted to the corresponding thiolester (96%, J = 4.0 Hz, in $CDCl_3$) by treatment with CH_3I (5 equiv, THF reflux for 2 h) followed by hydrolysis with 2 N HCl. The corresponding ester (57%, J = 4.2 Hz in $CDCl_3$)[21] is obtained by treatment of the thus obtained thiolester with 1.2 equiv of $NaOCH_3$ (CH_3OH, room temperature, 30 min). During these transformations, stereochemical configuration at C-2 is unchanged.

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(24) Gompper, R.; Elser, W. *Justus Liebigs Ann. Chem.* **1969**, *725*, 64.

(25) The stereochemistry of *erythro*- and *threo*-**4** was determined as the corresponding amides: Sucrow, W.; Richter, W. *Chem. Ber.* **1971**, *104*, 3679.

(26) The enolate **2a** (Na^+ gegenion), generated by treatment with $NaNH_2$ in liquid NH_3,[7] reacted with *trans*-crotyl bromide to provide *erythro*- and *threo*-**4** in a ratio of 73:24 (58% yield). All results presented here indicate that the previously assigned structure of ketene *S,N*-acetals is incorrect[7] and that the configuration should be *Z*.

(27) Bartlett, P. A.; Hahne, W. F. *J. Org. Chem.* **1979**, *44*, 882.

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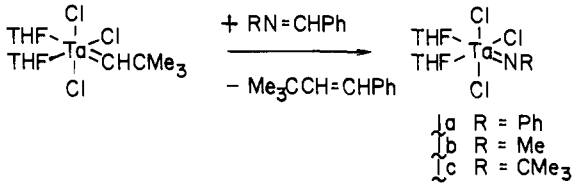
Tantalum Imido Complexes

Sir:

Only a few imido complexes of group 5 metals have been reported.[1] Three tantalum examples are $(R_2N)_3Ta{=}NR$,[2] $[Cl_3Ta{=}NC(R){=}]_2$,[3] and alkenylimido complexes prepared by reacting tantalum neopentylidene complexes with nitriles.[4] We have discovered that tantalum(V) alkylimido complexes can be prepared quantitatively from neopentylidene complexes and imines, a reaction which is related to the reaction of neopentylidene complexes with aldehydes, ketones, esters, and amides.[5] Since neopentylidene complexes are now available straightforwardly and in high yield,[6] this reaction provides a straightforward route to a variety of tantalum imido derivatives.

cis,mer-$Ta(CHCMe_3)(THF)_2Cl_3$, which can be prepared quantitatively from $Ta(CH_2CMe_3)_2Cl_3$ and THF,[6] reacts smoothly in a few minutes at room temperature in ether with RN=CHPh to give *cis*- and *trans*-$Me_3CCH{=}CHPh$ and the yellow (R = Ph) or white (R = Me or CMe_3) imido complexes **1** (eq 1), quanti-



(1)

(1) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

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