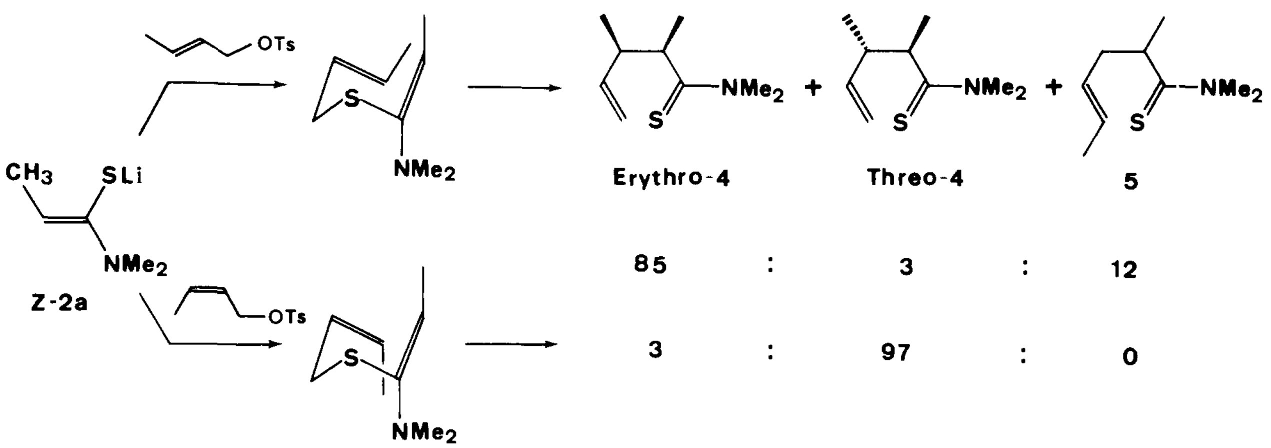
Scheme II



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 ^{1}H 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.

(21) Canceill, J.; Basselier, J. J.; Jaques, J. *Bull. Soc. Chim. Fr.* **1967**, 1024.

(22) Gaudemer, A. In "Stereochemistry" Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977.

(23) (a) Takahashi, H.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5803. (b) Takano, S.; Hirama, M.; Araki, T.; Ogasawara, K. *Ibid.* **1976**, *98*, 7084. (c) Tamaru, Y.; Harada, T.; Yoshida, Z. *Ibid.* **1980**, *102*, 2392.

(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*.

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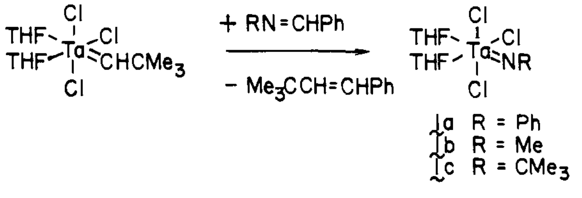
Tantalum Imido Complexes

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)

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

(2) Bradley, D. C. *Adv. Inorg. Radiochem.* **1966**, *9*, 315.

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(5) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399–5400.

(6) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236–6244.

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tatively.[7] It seems reasonable that a Ta═N bond should replace a Ta═C bond, since the often nearly linear metal–imido bond is closer to a triple bond than a double bond.[1] The cis,mer configuration for **1** is proposed on the basis of the presence of two types of THF ligands in the ^{1}H NMR spectra.

The reaction between **1a** and PMe$_3$ gives light yellow **2a** (eq 2). The cis,mer configuration of **2a** is based on inequivalence

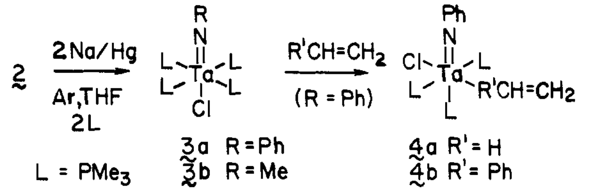
2a

(2)

of the PMe$_3$ ligands (−11.65 and −40.0 ppm in ^{31}P NMR spectrum at −30 °C) and faster exchange of one of them (we propose the one trans to the imido ligand) with added PMe$_3$ at temperatures above ~−30 °C. Interestingly, the orange PEt$_3$ derivative (**2b**) has a trans,mer geometry on the basis of its ^{31}P NMR spectrum (+15.5 ppm). A cis,fac geometry seems less likely but cannot be excluded by this data alone.

No ^{15}N NMR and few IR studies of labeled imido complexes have been reported.[1] The ^{15}N NMR spectrum[8a] of **1a**-^{15}N shows a peak at 369 ppm (referenced to liquid NH$_3$[8b]) while that for **2b**-^{15}N shows a singlet at 353 ppm. Coupling of ^{15}N to the two cis ^{31}P nuclei in **2b** evidently is small. In the IR spectrum of **1a** there is a medium-strength peak at ~1365 cm^{-1} and in the spectrum of **2b** at ~1345 cm^{-1}. The IR spectra of the ^{15}N-labeled complexes are identical with the unlabeled ones except these peaks are shifted to ~1335 and ~1315 cm^{-1}, respectively. The peak in the 1350-cm^{-1} region in each case is probably some combination of the Ta═N stretching mode coupled to the N—C stretching mode.[1,9]

The reduction of **2** with 2 equiv of sodium amalgam gives green **3a** in high yield (eq 3). This Ta(III) imido complex, like Ta(CHCMe$_3$)(PMe$_3$)$_4$Cl,[10] its carbon analogue, did not analyze well due to the lability of the PMe$_3$ ligands. Therefore it was identified by NMR methods.[11] The proposed structure is based on the coupling of the imidomethyl group in **3b** equally to four phosphorus nuclei (J_{HP} = 3.5 Hz). One PMe$_3$ ligand can be displaced readily from **3a** by ethylene or styrene to give **4**.[12] The structure of **4** is believed to be mer with Cl cis to the imido ligand since one and only one phosphine ligand (we propose the one trans to the imido ligand) is lost in solution and exchanges readily on the NMR time scale with added PMe$_3$. The olefin must lie in the TaL$_2$Cl plane since the two ethylene carbon atoms are identical in the ^{13}C NMR spectrum. The Ta═N—R stretching frequencies are proposed to be 1340 cm^{-1} in **3a** and 1355 cm^{-1} in **4a**, although these assignments need to be confirmed by ^{15}N labeling studies.



(3)

For some time we have been trying to prepare an imidoalkylidene complex in order to test whether the imido ligand, a good π-electron donor, would cause the alkylidene ligand to react with olefins to give metathesis products, just as alkoxide ligands apparently do.[13] Such a species can be prepared by using an organic azide,[1,14] as shown in eq 4. Complex **5**[15] is believed to be

5

(4)

structurally similar to bisneopentylidene complexes.[16] It sublimes at 120 °C and 1 μm without decomposing. It reacts slowly with ethylene (40 psi, 40 °C, 3 h) to give a quantitative yield of the two expected products of *rearrangement* of an intermediate metallacyclobutane complex, 4,4-dimethyl-1-pentene (80%), and *trans*-4,4-dimethyl-2-pentene (20%), but no metathesis products. It reacts with 1 equiv of acetone to give a 90% yield of 2,4,4-trimethyl-2-pentene[5] and a white, insoluble complex which shows a Ta═O stretch at ~835 cm^{-1} in the IR spectrum.

Complexes **1**–**4** react with ketones and aldehydes to give imines[17] in high yield (e.g., eq 5). The initial metal-containing

$$\underset{\mathbf{1a}}{\mathrm{Ta(NPh)(THF)_2Cl_3}} + \mathrm{PhCHO} \rightarrow \mathrm{PhCH{=}NPh} \qquad (5)$$

products probably are oxo analogues of the imido complexes, but none has been identified. (We believe that **5** reacts under mild conditions with acetone to give only 4,4-dimethylpentenes because the initial oxo complex is insoluble.) These results suggest that for "metathesis-like" reactions the preference for bonding to tantalum is O > NR > CHR.

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[7] Anal. R = Ph, Calcd for TaC$_{14}$H$_{21}$O$_2$Cl$_3$N: C, 32.17; H, 4.05. Found: C, 31.91; H, 3.99. R = CH$_3$, Calcd for TaC$_9$H$_{19}$O$_2$Cl$_3$N: C, 23.47; H, 4.16. Found: C, 23.09; H, 4.18. R = CMe$_3$, Calcd for TaC$_{12}$H$_{25}$O$_2$Cl$_3$N: C, 28.67; H, 5.01. Found: C, 28.81; H, 5.26.

[8] (a) Recorded at 9.04 MHz in benzene containing ~5% Cr(acac)$_3$ on a JEOL FX90Q spectrometer. (b) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979.

[9] We thank the referees for pointing this out.

[10] Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608–6609.

[11] For **3b**, ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 1.45 (t, 36, J_{HP} = 2.4, PMe$_3$), 2.96 (qt, 3, J_{HP} = 3.5 NCH$_3$). ^{31}P{^{1}H} (C$_6$D$_5$CD$_3$, 36 MHz): δ −7.8 (brs, s); ^{13}C{^{1}H} NMR (C$_6$D$_5$CD$_3$, 22 MHz, −20 °C) δ 22.2 (PMe$_3$), 48.0 (NCH$_3$).

[12] For **4a**, ^{1}H NMR (C$_6$D$_5$CD$_3$, 250 MHz) δ 1.19 (d, 9, PMe$_3$), 1.31 (t, 18, PMe$_3$), 1.58 (m, 2, C$_2$H$_4$), 1.77 (m, 2, C$_2$H$_4$), 6.49–6.94 (m, 5, phenyl); ^{31}P{^{1}H} NMR (C$_6$D$_5$CD$_3$, 36 MHz) δ −22.9 (t, J_{PP} = 14.6 Hz), −11.7 (d, J_{PP} = 14.6 Hz).

[13] Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G. A.; Fellmann, J. D. *J. Mol. Catal.* 1980, *8*, 73–83.

[14] (a) McGlinchey, M. J.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1265. (b) Cenini, S.; LaMonica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.

[15] ^{1}H NMR (C$_6$D$_6$, 250 MHz) δ 0.21 (s, 9, NSi*Me*$_3$), 1.16 (t, 18, J_{PH} = 3.3 Hz, PMe$_3$), 1.25 (s, 9, CHC*Me*$_3$), 7.98 (s, 1, C*H*CMe$_3$). ^{13}C NMR (C$_6$D$_6$, 22 MHz): δ 4.6 (q, J_{CH} = 126 Hz, NSiMe$_3$), 34.9 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 15.7 (t, J_{CH} = 126 Hz, PMe$_3$), 43.8 (s, CH*C*Me$_3$), 275.8 (d, J_{CH} = 99 Hz, *C*HCMe$_3$).

[16] (a) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

[17] Nugent noted that Ta(NR)(NR$_2$)$_3$ reacts with ketones to give imines: Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 578.

Tantalum Complexes Containing Diimido Bridging Dinitrogen Ligands

Sir:

There is no published example of a characterized dinitrogen complex containing a group 5 metal.[1] Here we show how several tantalum complexes containing a bridging dinitrogen ligand can

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[1] (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. (b) Chatt mentions[1a] that [Nb(dmpe)$_2$Cl]$_2$N$_2$ is obtained in low yield upon reducing Nb(dmpe)$_2$Cl$_4$ with Mg in THF under N$_2$ (Chatt, J.; Burt, R. J. Unpublished results).

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