A Novel Transmetalation Reaction: A Route to Transition Metallatranes

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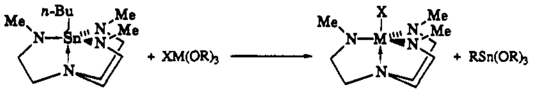
Transition metal amides have been extensively studied over the past three decades,[1] and they have recently drawn considerable interest as potential precursors for the synthesis of metal nitride thin films by chemical vapor deposition.[2] Our interest in such compounds has centered on those derived from symmetrical trifunctional amines which can be expected to confer volatility on the chelated metal. By employing $(H_2NCH_2CH_2)_3N$ (tren) a C_3 or C_{3v} structure such as $N{\vdots}Mo(HNCH_2CH_2)_3N$ could feature ligation of the metal by five rather than the normal four nitrogens. Our attempts to utilize the well-known transamination reaction of transition metal tris-dialkylamides[3] with tren and its trisubstituted methyl derivative $(MeHNCH_2CH_2)_3N$ gave only intractable polymeric materials, however.[4]

Here we report a high-yield synthetic route based on the novel transmetalation reaction 1.[5] The starting material **1** is easily made in high yield from *n*-$BuSn(NMe_2)_3$ and $(MeHNCH_2CH_2)_3N$ by a method[6] analogous to that used for $RSi(MeNCH_2CH_2)_3N$.[7]



(1)

1

2 MX = V=O

3 MX = Mo≡N

Although metathetical reactions of organostannanes were reported as early as the late 1960s by Lappert and co-workers,[8] no report on metathetical reactions involving transition metal alkoxides has appeared thus far. The azametallatranes **2** and **3** are both sublimable, highly moisture-sensitive, colored solids (red and yellow, respectively). Attempts to carry out reaction 1 with *n*-$BuSn(HNCH_2CH_2)_3N$, however, led to intractable reaction mixtures.

The AA′XX′ spectra of the methylene protons of the metallatrane cage of **2** and **3** appear as two sets of virtual triplets (virtual point group $3m$-C_{3v} at room temperature),[9] as has previously been observed for the analogous azasilatranes[7] and azastannatranes.[6] While azastannatranes possess $\Delta G_{T_c}{}^{\ddagger}$ values in the range 33–36 kJ/mol,[10] **2** and **3** exhibit values of 41.0 and 40.8 kJ/mol,[11] respectively, for the free activation enthalpies of racemization of the metallatrane framework (point group 3-C_3 at lower temperatures[12]). This suggests that **2** and **3** possess an unusually rigid metallatrane skeleton, which may be attributed to the presence of a transition metal. The high oxidation state of these metals would favor donation of the pseudoequatorial nitrogen lone pairs to the metal via π bonding. The π bonding between the metal and the multiply bonded apical atom (O in **2** and N in **3**) can be viewed as involving mainly the d_{xz} and d_{yz} AOs on the metal, leaving the $d_{x^2-y^2}$ and d_{xy} AOs for both σ and π bonding to the pseudoequatorial nitrogen. The latter interaction could be expected to inhibit rotational freedom around the M–N_{eq} bonds and would tend to maintain the plane of the π-bonding nitrogen and its substituent atoms coparallel with the V=O link. There would thus be a reduction in the flexibility of the five-membered rings compared with those in a main group analogue, such as the azastannatranes wherein N_{eq} π bonding is expected to be weaker.

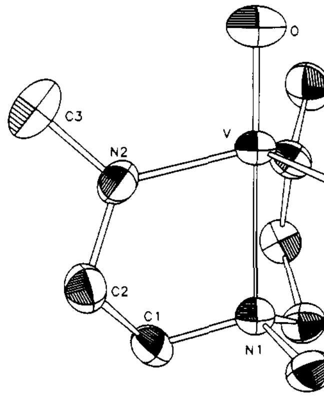


Figure 1. ORTEP drawing and atomic numbering scheme for **2**. Thermal ellipsoids are drawn at the 50% probability level. Pertinent bond distances (pm) and angles (deg) are as follows: V–O, 159.9 (6); V–N1, 232.1 (6); V–N2, 189.5 (3); N1–V–N2 78.8 (1).

Consistent with this view is the structure of **2** (Figure 1) determined by X-ray means[13] which displays an essentially trigonal planar geometry around the pseudoequatorial nitrogens (angle sum = 358.8 (8)°) with the planes coparallel with the O–V axis and puckered five-membered rings in a "paddle-wheel" arrangement. Whether the V–N_{eq} bond distance (189.5 (3) pm) is indicative of π bonding is difficult to determine owing to the absence of structural data for $V(V)NR_2$ compounds in the literature. Although the V–N_{ax} distance (232.1 (6) pm) is at the upper limit of the range observed for coordinated tertiary amines (mean distance = 227.7 pm[14]), a bonding interaction is clearly indicated. The V=O distance (159.9 (6) pm) is in the quoted range (155–162 pm[15]) as is the corresponding stretching frequency of 962 cm^{-1} (lit.[15] 875–1035 cm^{-1}). The Mo≡N stretching fre-

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(5) Solutions of $OV(O$-*i*-$Pr)_3$ (2.12 g, 8.70 mmol) and N≡Mo(O-*t*-$Bu)_3$ prepared according to the method of Chan et al. (Chan, D. M.-T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. C. *Inorg. Chem.* **1986**, *25*, 4170) (0.35 g, 1.1 mmol) in 50 mL of toluene with equimolar amounts of **1** were reacted at 70 °C for 5 h. After the solvent was removed in vacuo, the *n*-$BuSn(OR)_3$ was extracted with *n*-pentane and the solid residue washed twice with the same solvent. Sublimation at 80–100 °C (5 mTorr) gave pure **2** (80% yield; mp 175 °C dec): high-resolution MS calcd 252.11550, found 252.11498; FT-IR (KBr, cm^{-1}) 962 s, ν(V=O)). Anal. Calcd (found) for $C_9H_{21}N_4OV$: C, 42.86 (41.99); H, 8.39 (8.56); N, 22.21 (21.42). Sublimation under the same conditions gave **3** (70% yield; mp 130 °C dec): high-resolution MS calcd 291.08600, found 291.08662; FT-IR (KBr, cm^{-1}) 991 s, ν(Mo≡N)). Anal. Calcd (found) for $C_9H_{21}N_5Mo$: C, 36.61 (36.83); H, 7.17 (7.47); N, 23.72 (22.90).

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(9) ^1H NMR data (C_6D_6, 299.949 MHz) for **2**: 4.05 (s, 9 H, CH_3), 3.02 (unresolved due to $^3J_{VH}$, 6 H, $VNCH_2$), 2.32 (t, 6 H, $VNCH_2CH_2$, $^3J_{HH}$ = 5.7 Hz). **3**: 4.09 (s, 9 H, CH_3), 2.86 (t, 6 H, $MoNCH_2$, $^3J_{HH}$ = 5.6 Hz), 2.11 (t, 6 H, $MoNCH_2CH_2$, $^3J_{HH}$ = 5.6 Hz).

(10) Plass, W.; Verkade, J. G. Manuscript in preparation.

(11) Free activation enthalpies $\Delta G_{T_c}{}^{\ddagger}$ were calculated from the coalescence temperature of the $MNCH_2$ protons (toluene-d_8, 299.949 MHz). **2**: T_c = 215.5 ± 1 K, $\Delta\nu$ = 236 ± 10 Hz. **3**: T_c = 213.0 ± 1 K, $\Delta\nu$ = 196 ± 10 Hz.

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(13) A suitable crystal was obtained by crystallization from toluene at −20 °C. Crystal data: trigonal space group *R*3*c* (No. 161), a = 1154.3 (1) pm, c = 1551.1 (2) pm, $V = 1789.8\ (6) \times 10^6\ pm^3$, Z = 6, d_{calcd} = 1.203 g/cm^3, μ(Mo Kα) = 7.9 cm^{-1}; crystal dimensions $0.20 \times 0.15 \times 0.12\ mm^3$; 458 unique reflections observed, 345 with $F_o{}^2 > 3\sigma(F_o{}^2)$. The choice of space group was suggested by intensity statistics and was confirmed by successful refinement. The structure was solved by direct methods. The hydrogen atoms were used in idealized positions for structure factor calculations. Refinement of 45 parameters converged with an agreement factor of R = 0.019 and R_w = 0.027 with $\omega^{-1} = \sigma^2(F_o)$. The data were collected at room temperature on an Enraf-Nonius CAD4 instrument, with the crystal sealed in a capillary tube. The refinement was carried out with the SHELXS-86 package.

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(15) Nugent, W. A.; Mayer, J. M. *Metal Ligand Multiple Bonds*; Wiley and Sons: New York, 1988.

(16) ^{13}C NMR data were obtained in C_6D_6 at 75.429 MHz (atom numbering in Figure 1). **2**: 60.32 (C2, $^2J_{VC}$ = 7.2 Hz), 55.51 (C3, $^2J_{VC}$ = 4.5 Hz), 51.50 (C1, $^2J_{VC}$ = 2.4 Hz). **3**: 58.87 (C2), 58.44 (C3), 49.98 (C1).

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quency (991 cm^{-1}) is also within the given range (948–1109 cm^{-1}[15]).

The fact that the ^{51}V NMR spectrum of **2** reveals an increase in shielding for the solution state (C_6D_6, 78.86 MHz: −240.9 ppm relative to external $OVCl_3$) versus the solid state (MAS 78.86 MHz: −205.5 ppm) may be taken to suggest that the $V{-}N_{ax}$ bond is stronger in the solution state, in conformity with the relatively strong rigidity of the metallatrane frameworks of **2** (and **3**) found in solution. Interestingly, the $^{13}C\{^1H\}$ spectrum[15] of **2** reveals clearly resolved V–C couplings (rarely observed[17]) for which the 7.2-Hz two-bond coupling involving C2 is the largest. The properties of **2** and **3** as CVD agents and the applicability of transmetalation reaction 1 to other transition metals as well as other ligand systems are currently under investigation.

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Supplementary Material Available: Tables of complete crystal structure data, bond lengths and angles, and positional and anisotropic thermal parameters (5 pages); a listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Enantioselective Catalytic Isomerization of an Unfunctionalized Achiral Alkene

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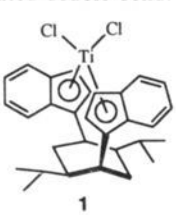
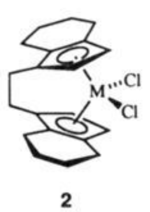
Asymmetric catalytic reactions using functionalized substrates such as the epoxidation of allylic alcohols[1] or hydrogenation of dehydroalanines[2] have had spectacular successes over the past decade, yet the development of catalysts for asymmetric reactions involving relatively unfunctionalized substrates remains an important challenge. Although catalysts have been reported for the highly enantioselective double-bond isomerization of allylic amines,[3] similar success using an isolated double bond have not been reported. We report here the development of the new chiral bis(indenyl)titanium catalyst **1** containing a chiral bridging group and its application in the first highly enantioselective isomerization of an isolated double bond.



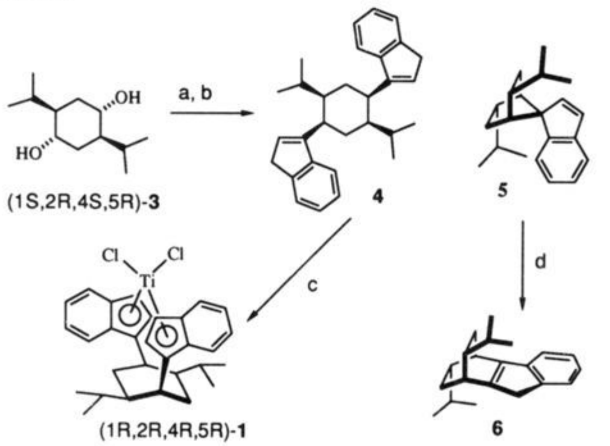
1



2

Chiral *ansa*-bis(indenyl)metal complexes are emerging as an important class of catalysts for asymmetric hydrogenation[4a] and stereoregular polymerizations[4b] and as a reagent for the asymmetric synthesis of allylic amines.[4c] The most common complexes of this type are the ethylene-bridged *ansa*-bis(tetrahydroindenyl)zirconium and -titanium dichlorides **2** prepared from the 1,2-ethylenebis(1-indenyl) ligand by Brintzinger.[5] Since the two faces of each indenyl ligand are enantiotopic in the ethylene-bridged ligand, metalation generally produced a mixture of meso and *dl* isomers from which the desired C_2-symmetric complex had to be separated and resolved. In an effort to simplify the synthesis of enantiomerically enriched bis(indenyl)metal complexes, we have developed *ansa*-bis(indenyl)metal complexes containing chiral, enantiomerically pure bridging groups.[6] By introducing chirality

Scheme I[a]



[a] Reagents and conditions: (a) MsCl, Et_3N, 0 °C; (b) indenyllithium, Et_2O, 0–23 °C, 12 h (60% of **4**); (c) (i) *n*-butyllithium, THF −78 to 0 °C, 0.5 h, 23 °C, 0.5 h; (ii) $TiCl_3$, −78 to 65 °C, 12 h; (iii) 6 N HCl, $CHCl_3$, air, −78 to 23 °C, 2 h; (d) 280 °C, 24 h.

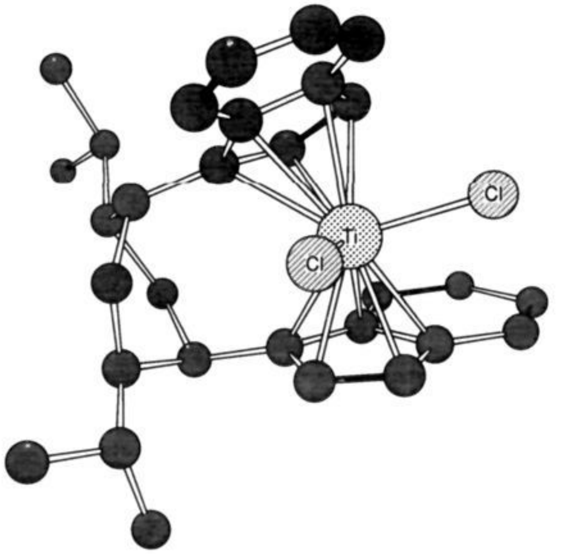


Figure 1. Solid-state structure of **1** determined by X-ray diffraction.

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