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Multicenter Ligand Transformations. Hydrogenation with a Trans Stereochemistry. Synthesis of $Re_2(CO)_8$[*trans*-μ-Me(H)C=C(H)NMe_2] by the Addition of Hydrogen to $Re_2(CO)_8(\mu\text{-MeC}{\equiv}\text{CNMe}_2)$

Richard D. Adams,* Gong Chen, and Jianguo Yin
Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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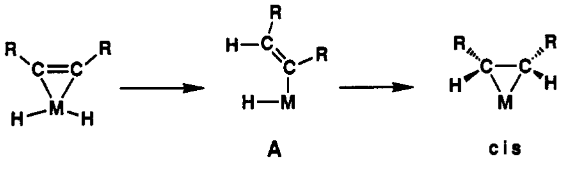
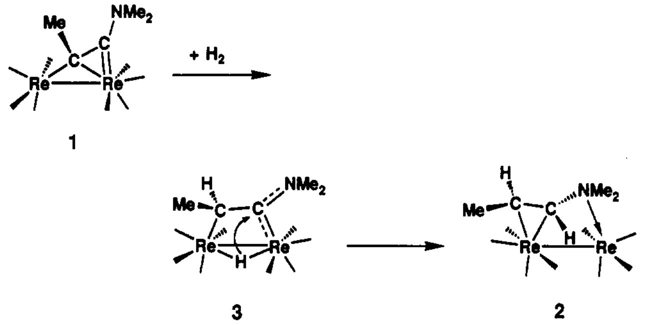
Summary: The reaction of $Re_2(CO)_8(\mu\text{-MeC}{\equiv}\text{CNMe}_2)$ (**1**) with hydrogen yields the enamine ligand complex $Re_2(CO)_8$[*trans*-μ-Me(H)C=C(H)NMe_2] (**2**; 41% yield) via the partially hydrogenated ligand-bridged intermediate $Re_2(CO)_8[\mu\text{-Me(H)CC(NMe}_2)](\mu\text{-H})$ (**3**). A direct route to trans stereochemistry at the coordinated C=C bond in **2** is attributed to a mechanism that depends on the binuclear coordination of the partially hydrogenated ligand.

The hydrogenation of alkynes by mononuclear metal complexes usually proceeds via σ-alkenyl intermediates (A) to yield alkenes that contain the cis or *E* stereochemistry (eq 1).[1] The stereochemistry of the alkene is usually defined upon formation of the intermediate since the cis–trans (*E*–*Z*) isomerization about the C–C double bond in the alkenyl ligand is generally a high-energy process.[2,3] It is believed that multicenter interactions in polynuclear metal complexes may permit new and facile ligand transformations that are not accessible to mononuclear metal complexes.[4] Herein, we provide evidence that the addition of hydrogen to the ynamine ligand in the dirhenium complex $Re_2(CO)_8(\mu\text{-MeC}{\equiv}\text{CNMe}_2)$ (1)[5] yields the product $Re_2(CO)_8$[*trans*-μ-Me(H)C=C(H)NMe_2] (2) via the *ligand-bridged intermediate* $Re_2(CO)_8[\mu\text{-Me(H)}\text{-}\text{CC(NMe}_2)](\mu\text{-H})$ (3), which leads directly to 2.



(1)

Scheme I



Compound 2 was obtained in 41% yield by the reaction of 1 with H_2 (1 atm) in refluxing heptane solvent for 35 min.[6] Compound 2 appears to be the first example of a

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(1) (a) Muetterties, E. L. *Inorg. Chim. Acta* **1981**, *50*, 1. (b) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: Oxford, U.K., 1982; Chapter 51.1.6.

(2) There are a few cases where the cis–trans isomerizations of σ-alkenyl ligands under mild conditions have been documented.[3]

(3) (a) Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917. (b) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410.

(4) (a) Adams, R. D. In *Metal–Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Jr., Ed.; Plenum: New York, 1990; pp 75–89. (b) Chisholm, M. H. *Ibid.*, pp 55–74. (c) Adams, R. D.; Horvath, I. T. Prog. *Inorg. Chem.* **1985**, *33*, 127.

(5) Adams, R. D.; Chen, G.; Yin, J. *Organometallics* **1991**, *10*, 1278.

(6) IR ν(CO) (cm^{-1}) for 2 in hexane: 2086 (w), 2040 (w), 1989 (s), 1967 (m), 1932 (m). ^1H NMR (δ) for 2 in $CDCl_3$: 4.28 (d, CH, $^3J_{H-H}$ = 10.5 Hz), 3.26 (s, 3 H, NMe), 2.25 (s, NMe), 2.17 (dq, CH, $^3J_{H-H}$ = 10.5 Hz, $^3J_{H-H}$ = 5.7 Hz), 2.06 (d, CMe, $^3J_{H-H}$ = 5.7 Hz). Satisfactory elemental analyses for C, H, and N have been obtained. The mass spectrum for 2 shows the parent ion plus ions corresponding to the loss of each of eight CO ligands. Small amounts (6% yield) of a product of further hydrogenation formulated as $Re_2(CO)_8[\mu\text{-Et(H)C(NMe}_2)](\mu\text{-H})$ were also obtained. Spectra for $Re_2(CO)_8[\mu\text{-Et(H)C(NMe}_2)](\mu\text{-H})$: IR ν(CO) (cm^{-1}) in hexane 2107 (w), 2076 (m), 2003 (vs), 1984 (m), 1960 (s), 1951 (m); ^1H NMR (δ) in $CDCl_3$ 3.25 (dd, 1 H, J_{H-H} = 2.1 Hz), 3.08 (s, 3 H), 2.18 (m, 1 H), 1.68 (m, 1 H), 0.88 (t, 3 H, $^3J_{H-H}$ = 7.2 Hz), −14.44 (s, 1 H).

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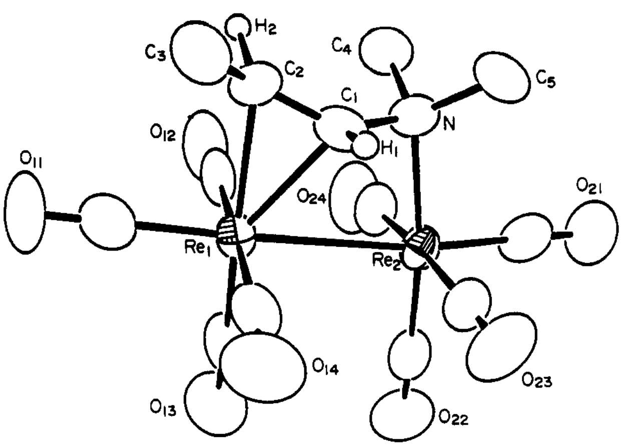

Figure 1. ORTEP diagram of $Re_2(CO)_8$[*trans*-μ-Me(H)C=C(H)NMe_2] (**2**). Selected interatomic distances (Å) and angles (deg): Re(1)–Re(2) = 3.024 (1), Re(1)–C(1) = 2.34 (1), Re(1)–C(2) = 2.37 (1), Re(2)–N = 2.224 (9), C(1)–N = 1.46 (1), C(1)–C(2) = 1.37 (1); C(2)–C(1)–N = 130 (1).

cluster complex containing an enamine ligand and was therefore structurally characterized by crystallographic methods.[7,8] The molecular structure of **2** is shown in Figure 1. The olefinic portion is coordinated through its π-bond to Re(1), while the amino group is coordinated to Re(2). The Re(1)–Re(2) distance, 3.024 (1) Å, is typical of a Re–Re single bond.[5]

When the reaction of **1** with hydrogen (10 atm) was performed in hexane solvent at 70 °C in a high-pressure reaction vessel for 70 min, the product $Re_2(CO)_8$[μ-Me(H)CC(NMe_2)](μ-H) (**3**) was obtained in 13% yield with only small amounts of **2**.[9] The structure of **3** was established by crystallographic methods and is shown in Figure 2.[7,10] The molecule contains two $Re(CO)_4$ groups joined by a hydride-bridged metal–metal bond (Re(1)–Re(2) = 3.1944 (8) Å). There is a NMe_2-substituted alkenyl ligand that bridges the metal atoms with C(1) coordinated to Re(1) and C(2) coordinated to Re(2). The nitrogen atom is planar, and the C(1)–N bond has multiple-bond character (C(1)–N = 1.32 (1) Å).[11] Compound **3** was isomerized cleanly to **2** (isolated yield 93%) by heating to 60 °C for 6 h. No intermediates were observed when the reaction was followed by ^1H NMR spectroscopy in an NMR tube in toluene-d_8. It is believed that the direct transformation of the aminoalkenyl ligand in **3** to the trans enamine in **2** is made possible to a large degree by the μ-η^2 coordination of the ligand, which prevents it from achieving the rigid cis (*E*) stereochemistry that is established for σ-alkenyl ligands in the first stages of hydrogenation by mononuclear metal complexes (A). Indeed, the large C(3)–C(2)–C(1)–N torsion angle (106°) shows that a significant transformation toward the trans stereochemistry has already occurred and that a smooth transition to **2** should be expected. The intramolecular character of the **3** to **2** transformation was established by a crossover experiment.[13] The nature of the hydrogen activation step and formation of **3** is not yet clear, but some cluster complexes containing metal–metal bonds have been shown to activate hydrogen without the usual ligand dissociation required to produce a vacant coordination site.[14] The complete sequence of transformations is shown in Scheme I, where the arrow shows the anticipated shift of the hydride ligand to the carbon atom to form **2**.

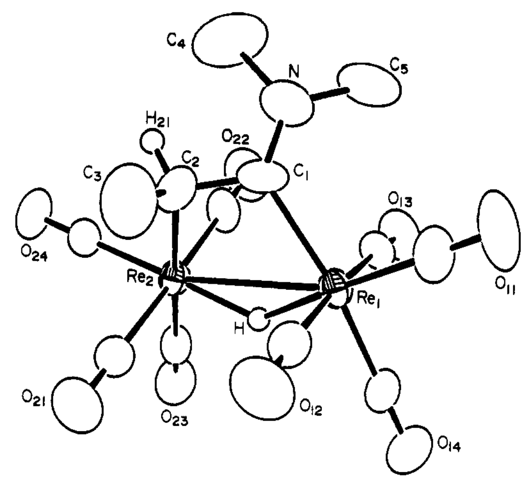

Figure 2. ORTEP diagram of $Re_2(CO)_8$[μ-Me(H)CC(NMe_2)](μ-H) (**3**). Selected interatomic distances (Å) and angles (deg): Re(1)–Re(2) = 3.1944 (8), Re(1)–C(1) = 2.21 (1), Re(2)–C(2) = 2.26 (1), C(1)–C(2) = 1.45 (2), C(1)–N(1) = 1.32 (1), Re(1)–H = 1.83 (8), Re(2)–H = 1.73 (8); C(2)–C(1)–N = 117 (1).

Several years ago Muetterties proposed that bridging alkyne ligands could be transformed to alkenyl ligands with a trans stereochemistry in a single step by an intramolecular hydrogen-transfer process that was proposed to be intrinsically binuclear in its metal interactions.[1a] Shortly thereafter, he documented the first and only example of such a transformation.[15] Our studies provide details of a new variation of the Muetterties transformation and demonstrate that it is also intrinsically binuclear in character.

Acknowledgment. These studies were supported by the U.S. Department of Energy under Grant No. DEFG84ER13296. A Bruker AM-500 NMR spectrometer was purchased with funds from the National Science Foundation under Grant No. CHE-8904942.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for both of the structural analyses (14 pages); tables of structure factors (25 pages). Ordering information is given on any current masthead page.

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(7) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. Structure solutions and refinements were made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX.

(8) Crystal data for **2**: space group $P2_1/n$, $a = 7.686$ (2) Å, $b = 16.372$ (4) Å, $c = 14.080$ (3) Å, $\beta = 100.43$ (1)°, $Z = 4$, 1652 reflections, $R = 0.026$.

(9) In the 70-min reaction period most (>50%) of the **1** is unreacted. With longer reactions periods the yield of **2** is increased greatly and the yield of **3** is much smaller. Spectra for **3**: IR ν(CO) (cm^{-1}) in hexane 2086 (w), 2040 (m), 1989 (s), 1967 (m), 1932 (m); ^1H NMR (δ) in $CDCl_3$ 3.57 (q, 1 H, C*H*Me, $^3J_{H-H} = 6.6$ Hz), 3.51 (s, br, 6 H, NMe_2), 2.00 (d, 3 H, CH*Me*, $^3J_{H-H} = 6.6$ Hz), −15.29 (s, Re*H*). Satisfactory elemental analyses for C, H, and N have been obtained.

(10) Crystal data for **3**: space group $P2_1/n$, $a = 9.384$ (2) Å, $b = 18.786$ (4) Å, $c = 10.188$ (1) Å, $\beta = 100.98$ (1)°, $Z = 4$, 1807 reflections, $R = 0.023$. The hydride ligand was located and refined crystallographically.

(11) In accord with previous work on ynamine ligands,[5,12] this ligand could also be described as a metalated ethyl(dimethylamino)carbene ligand.

(12) (a) Adams, R. D.; Tanner, J. T. *Organometallics* **1988**, *7*, 2241. (b) Adams, R. D.; Chen, J. T.; Tanner, J. T.; Yin, J. *Organometallics* **1990**, *9*, 1523. (c) Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansen, O. *J. Organomet. Chem.* **1986**, *310*, 367.

(13) An equimolar mixture of $Re_2(CO)_8$[μ-Me(H)CC(NMe_2)](μ-H) and $Re_2(CO)_8$[μ-Me(D)CC(NMe_2)](μ-D) was transformed to **2**. A mass spectral analysis of the product **2** showed that it consisted of $Re_2(CO)_8$[*trans*-μ-Me(H)C=C(H)NMe_2] and $Re_2(CO)_8$[*trans*-μ-Me(D)C=C(D)NMe_2]. No significant amounts of the mixed 1 H/1 D forms of **2** were formed by crossover.

(14) (a) Adams, R. D.; Wang, S. *Organometallics* **1986**, *5*, 1272. (b) Adams, R. D.; Wang, S. *Inorg. Chem.* **1986**, *25*, 2534. (c) Arif, A. M.; Bright, T. A.; Jones, R. A.; Nunn, C. M. *J. Am. Chem. Soc.* **1988**, *110*, 6894.

(15) Burch, R. R.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 4257.