## SUPPLEMENTARY MATERIAL FOR

Trapping the Dirhenium Alkynyl Fischer Type Carbenes through Michael Addition. Unexpected Room Temperature E/Z Isomerization of  $(CO)_5Re(CO)_4Re=C(OMe)C(H)=C(NMe_2)(SiMe_3).$ 

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## **Experimental Section**

General Experimental Data. All reactions were conducted under N<sub>2</sub> atmospheres. Chemicals were treated as follows: THF, distilled from CuCl, predried over NaOH, and then distilled from Na/benzophenone; Et<sub>2</sub>O, hexanes, distilled from Na/benzophenone; MeOH (POCh), Re<sub>2</sub>(CO)<sub>10</sub> (Aldrich), TMSC=CH (Aldrich), *n*-BuLi (2.5M soln in hexanes; Aldrich), Me<sub>3</sub>O<sup>+</sup> BF<sub>4</sub><sup>-</sup> (Aldrich), MeOTf (Aldrich), HNMe<sub>2</sub> (2.0M soln in THF; Aldrich), KF (Aldrich), NH<sub>4</sub>OH (POCh), and NaHCO<sub>3</sub> (POCh) used as received.

IR spectra were recorded on Mattson Polaris FT spectrometer. NMR spectra were obtained on Varian 300 spectrometer. Mass spectra were recorded on Finningan MAT 95 high resolution instrument. Microanalyses were conducted by Atlantic Microlab.

**Re**(**CO**)<sub>5</sub>**Re**(**CO**)<sub>4</sub>(=**C**(**OMe**)**C**=**CTMS**) (1). A 50 mL Schlenk flask was charged with TMSC=CH (0.020 mL, 0.142 mmol), Et<sub>2</sub>O (15 mL), and THF (15 mL). The solution was cooled in a CO<sub>2</sub>/acetone bath to -78 °C and 2.5 M solution of *n*-BuLi (0.057 mL, 0.142 mmol) was added with stirring. After 1 h Re<sub>2</sub>(CO)<sub>10</sub> (0.093 g, 0.142 mmol) was added and solution was gradually warmed up to room temperature. After another 30 min the solution was cooled to -78 °C and Me<sub>3</sub>O<sup>+</sup> BF<sub>4</sub><sup>-</sup> (0.063 g, 0.426 mmol) was added. After 30 min the mixture was warmed to room temperature and allowed to stir for an additional 30 min. The solvent was removed *in vacuo*. Chromatography (Florisil washed with aq. NH<sub>4</sub>OH; 5:1 v/v hexanes/THF) gave orange band which was collected and kept at -30 °C to give orange solid containing 1. IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) v<sub>CO</sub> and v<sub>C=C</sub>: 2104 w, 2094 w, 2071 s, 2048 m, 2008 s, 1967 s. <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 3.39 (s, OMe), 0.12 (s, TMS). MS (positive Cs-FAB, 3-NBA/CH<sub>2</sub>Cl<sub>2</sub>) 764 (M<sup>+</sup>, 38%), 736 (M<sup>+</sup>-CO, 35%), 708 (M<sup>+</sup>-2CO, 32%), 680 (M<sup>+</sup>-3CO, 100%), 652 (M<sup>+</sup>-4CO, 76%) ; no other peaks above 500 of>30%.

 $(CO)_5Re(CO)_4Re(=C(OMe)CH=C(NMe_2)TMS)$  (2). A 50 mL Schlenk flask was charged with TMSC=CH (0.020 mL, 0.142 mmol), Et<sub>2</sub>O (15 mL), and THF (15 mL). The solution was cooled in a CO<sub>2</sub>/acetone bath to -78 °C and 2.5 M solution of *n*-BuLi (0.057 mL, 0.142 mmol) was added with stirring. After 1 h Re<sub>2</sub>(CO)<sub>10</sub> (0.093 g, 0.142 mmol) was added and solution was gradually warmed up to room temperature. After another 30 min the solution was cooled to 0 °C and 0.016 mL of MeOTf (0.046 g, 0.284 mmol) was added. After 30 min the mixture was cooled to -130 °C and 2.0 M solution of HNMe<sub>2</sub> (0.213 mL, 0.426 mmol) was added dropwise. After 30 min the cold reaction was quenched with water. Solvent from red organic layer was evaporated *in vacuo* giving red-brown residue. Chromatography (Florisil washed with aq. NH<sub>4</sub>OH; 4:1 v/v hexanes/THF) gave red-orange band. The solvent was removed *in vacuo* yielding **2** in 82% yield. Calcd. for  $C_{18}H_{19}NO_{10}Re_2Si$ : C, 26.70; H, 2.36. Found: C, 26.67 (26.63); H, 2.29 (2.32). <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 6.25 (s, 1H), 3.95 (s, 3H of OMe), 3.13 (s, 6H of NMe<sub>2</sub>), 0.32 (s, 9H of TMS). MS (positive Cs-FAB, 3-NBA/CH<sub>2</sub>Cl<sub>2</sub>) 809 (M<sup>+</sup>, 13%), 484 (M<sup>+</sup>-Re(CO)<sub>5</sub> 100%) 456 (M<sup>+</sup>-Re(CO)<sub>5</sub>-Si, 40%), 426 (M<sup>+</sup>-Si-Me<sub>2</sub>, 27%); no other peaks above 300 of>10%.

(CO)<sub>5</sub>Re(CO)<sub>4</sub>Re(=C(OMe)C(H)=C(H)NMe<sub>2</sub>) (3). A 250 mL Schlenk flask was charged with **4** (0.100 g, 0.123 mmol) and 80 mL of THF/MeOH (1:1) mixture. KF (0.030 g, 0.181 mmol) was added to the solution and the mixture was stirred for 2 h. Then, 150 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the yellow solution was extracted with two 100 mL portions of water. Solvent from yellow organic layer was removed *in vacuo* giving crude yellow material. Chromatography (Florisil washed with aq. NH<sub>4</sub>OH; 4:1 v/v hexanes/THF) gave yellow band. The solvent was removed *in vacuo* giving **3** in 71% yield. Calcd. for C<sub>15</sub>H<sub>11</sub>NO<sub>10</sub>Re<sub>2</sub>: C, 24.42; H, 1.50. Found: C, 24.41 (24.34); H, 1.47 (1.51). <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>) 8.83 (d, J<sub>HH</sub> = 11.4 Hz, 1H from *cis*), 8.13 (br, d, J<sub>HH</sub> = 11.7 Hz, 1H from *trans*), 6.05 (d, J<sub>HH</sub> = 11.4 Hz, 1H from *cis*), 5.78 (br, d, J<sub>HH</sub> = 11.7 Hz, 1H from *trans*), 3.92 (s, 3H of OMe from *cis*), 3.83 (s, 3H of OMe from *trans*), 3.37 (s, 3H of NMe<sub>2</sub> from *cis*), 3.35 (s, 3H from NMe<sub>2</sub> from *trans*), 3.11 (s, 3H of NMe<sub>2</sub> from *cis*), 3.05 (s, 3H from NMe<sub>2</sub> from *trans*). MS (positive Cs-FAB, 3-NBA/CH<sub>2</sub>Cl<sub>2</sub>) 737 (M<sup>+</sup>, 100%); no other peaks above 420 of>20%.

(CO)<sub>5</sub>Re(CO)<sub>4</sub>Re(=C(NMe<sub>2</sub>)C=CTMS) (4). A 100 mL Schlenk flask was charged with TMSC=CH (0.050 mL, 0.354 mmol), Et<sub>2</sub>O (25 mL), and THF (2 mL). The solution was cooled in a CO<sub>2</sub>/acetone bath to -78 °C and 2.5 M solution of *n*-BuLi in hexane (0.170 mL, 0.425 mmol, 1.2 eq) was added. After stirring the solution for 1 h at 0 °C it was cooled down to -78 °C and Re<sub>2</sub>(CO)<sub>10</sub> (0.277 g, 0.425 mmol) was added. The solution was gradually warmed up to room temperature. After another 1 h stirring the solution was cooled to 0 °C and 0.080 mL of MeOTf (0.116 g, 0.707 mmol) was added. After 30 min the mixture was cooled to -130 °C and 2.0 M solution of HNMe<sub>2</sub> in THF (0.530 mL, 1.060 mmol) was added dropwise. After 30 min H<sub>2</sub>O was added and the mixture was very slowly warmed up to room temperature. Yellow organic layer was

separated and the solvent was removed *in vacuo*. The brown-yellow residue was dissolved in hexane/THF mixture (4/1) and chromatographed (Florisil washed with aq. NH<sub>4</sub>OH; 4:1 v/v hexane/THF) giving orange-yellow band. The solvent was removed *in vacuo* giving yellow compound in 79% yield. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 3.60 (s, 3 H of NMe<sub>2</sub>) and 3.57 (s, 3 H of NMe<sub>2</sub>), 0.21 (s, 9H of SiMe<sub>3</sub>).

(CO)<sub>5</sub>Re(CO)<sub>4</sub>Re(=C(NMe<sub>2</sub>)C=CH) (5). A 100 mL Schlenk flask was charged with 1 (0.190 g, 0.235 mmol) and 30 mL of MeOH/THF mixture (1/1 v/v). Then KF (0.007 g, 0.122 mmol) was added and mixture was stirred for 1 h at room temperature. At this time 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the yellow solution was extracted with 50 mL of a saturated aqueous NaHCO<sub>3</sub> solution. The yellow organic layer was separated and solvent was evaporated *in vacuo*. The yellow residue was dissolved in hexanes/THF mixture (4/1) and chromatographed (Florisil washed with aq. NH<sub>4</sub>OH; 4:1 v/v hexanes/THF) giving yellow band. The solvent was removed *in vacuo* giving yellow **5**. IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 2099 (w), 2071 (m), 2039 (m), 2012 (s), 1996 (m), 1981 (m), 1968 (m), 1923 (w). <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 5.28 (s, 1H from C=C<u>H</u>), 3.67 (s, 3 H of NMe<sub>2</sub>), 3.63 (s, 3 H of NMe<sub>2</sub>).

**Crystallography**. Data were collected on **2** and **3** as outlined in Table 1. Cell constants were obtained from 50 reflections for **2** and **3** ( $10^{\circ} < \theta < 16^{\circ}$ ). Space groups were determined from systematic absences (h0l h+l=2n; none) and subsequent least-squares refinement. Standard reflections (every 100 scans) showed no decay. Lorentz and polarization corrections were applied. The structures were solved by standard direct methods and refined by full-matrix-least squares on F<sup>2</sup> using SHELXTL Package.<sup>S1</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and added to the structure factor calculations. Scattering factors, and  $\Delta f'$  and  $\Delta f''$  values, were taken from the literature.<sup>S2</sup> Additional data for structure collection and refinement are in the manuscript references and Table S1 below.

Complex	2	3
F(000)	3024	676
Crystal dimensions, mm	0.4 x 0.4 x 0.4	0.4 x 0.3 x 0.3
Reflections measured	7435	3625
Index ranges (h, k, l)	0, 13; 0, 14; -36, 36	0, 10; -11, 11; -13, 13
Range for data collection, deg	2.01-23.10	2.13-25.05
Reflection measured	7435	3625
Independent reflection number	7036	3493
Observed data, $>2\sigma(I)$	4439	2729
No. of variables	577	253
Goodness of fit	1.542	1.446
R <sub>int</sub>	0.0312	0.0191
$R = \Sigma   F_o  -  F_c   / \Sigma  F_o $ (obs., all)	0.0429, 0.1102	0.0296, 0.0459
$wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w[F_o^4]^{1/2} \text{ (obs., all)}$	0.1609, 0.2039	0.0872, 0.0921
$\Delta/\sigma$ (max)	0.000	0.000
$\Delta/\rho$ (min), e/Å <sup>3</sup>	-1.94	-1.81
$\Delta/\rho$ (max), e/Å <sup>3</sup>	1.87	0.96

## Table S1. Summary of Crystallographic Data.

<sup>[a]</sup> Data common to all structures: (a) Temperature of collection (K), 298(1); (b) Diffractometer, KUMA KM4; (c) Radiation (Å), Mo  $K_{\alpha}$  (0.71073); (d) Data collection method,  $\omega$ -2 $\theta$ .



<sup>1</sup>H NMR spectrum of **1** (disregard signal at 0.431 ppm).



FAB-MS of 1.



Isotope pattern for parent ion of **1**.



<sup>1</sup>H NMR spectrum of **2**.



<sup>1</sup>H NMR spectrum of **2** and **4** mixture.



<sup>1</sup>H NMR spectrum of **3**.

(S1) Sheldrick, G. M. SHELXTL ver. 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

(S2) Cromer, D. T.; Waber, J. T. in *International Tables for X-ray Crystallography*, *Volume IV, tables 2.2B and 2.3.1* (Eds.: J. A. Ibers, W. C. Hamilton), Kynoch, Birmingham, England, **1974**.