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Supporting Information

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N-Heterocyclic Carbene-Copper(I)-Catalyzed Carboxylation of Organoboronic Esters.

Takeshi Ohishi, Masayoshi Nishiura and Zhaomin Hou*

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama, 351-0198, Japan

E-mail: houz@riken.jp

Experimental Section

General Methods. Unless otherwise noted, all reactions were performed under a dry nitrogen or argon atmosphere using Schlenk-line techniques or under nitrogen atmosphere in an Mbraun glovebox. Argon and nitrogen were purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 A) catalyst unit. The concentration of the oxygen and moisture in the glovebox was always kept below 0.1 ppm (monitored by an Mbraun O_2/H_2O Combi-Analyzer). Dry THF, toluene, and hexane were dried by Mbraun SPS-800 and stored over fresh Na chip in the glovebox. Flash column chromatography was conducted on silica gel 60 N, 40-50 μm (Kanto Chemical Co.). The NMR spectra of an air and moisture sensitive compounds were recorded by using of J. Young NMR tube (Wilmad 528-JY). ^{1}H NMR and ^{13}C NMR were recorded on a JEOL-AL400 or a JNM-AL300 spectrometer. Elemental analyses were performed by a MICRO CORDER JM10. Carbon dioxide, commercially available arylboronic acids and other all reagents were used without further purification.

Synthesis of NHC ligand and [(IPr)CuCl]

IPr·HCl,[1] IMes·HCl,[1] and [(IPr)CuCl][2] were prepared according to the literatures, using *t*BuOK instead of *t*BuONa.

Synthesis of organoboronic esters

Method A: Arylboronic esters **1a**[3], **1b**[3], **1c**[4], **1d**[5], **1g**[6], **1h**, **1i**[3], **1j**[7], **1k**[5], **1l**[8], **1m**[9], **1n**[10], **1o**[5], **1p**[11], **1q**[12], **1r**[5], **1s**[5], **1t**[5], **1u** were prepared by esterification of the corresponding arylboronic acids with 2,2-dimethyl-1,3-propanediol[13]

Method B: Arylboronic esters **1e, 1w** were prepared from the corresponding bromobenzene derivatives according to the literature procedure, using 2,2-dimethyl-1,3-propandiol instead of

ethyleneglycol[13].

Method C: Arylboronic ester **1f** was prepared from the corresponding diol derivative according to the literature procedure [14].

Method D: Arylboronic ester **1v** was prepared from the corresponding diol derivatives according to the literature procedure[15].

Preparation of alkenylboronic esters

Method E: Alkenylboronic esters **1x, 1y,** and **1z** were prepared by hydroboration of alkyne followed by transesterification.[16]

General procedure for (IPr)Cu-catalyzed carboxylation of organoboronic esters

A solution of *t*BuOK (1.05 mmol, 1.05 mL of *t*BuOK in 1M solution of THF) was added by a syringe to a stirred solution of [(IPr)CuCl] (4.8 mg, 1 mol%) and organoboronic ester (1 mmol) under N_2 at room temperature. CO_2 (balloon) was introduced, and the reaction mixture was then heated at 70 ˚C for 24 h. The reaction mixture was acidified by 1M solution of hydrochloric acid, and the aqueous phase was exstracted with ethyl acetate (3 times). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding carboxylic acid.

Carboxylic acids **2a**, **2b**, **2c**, **2d**, **2g**, **2h**, **2i**, **2j**, **2k**, **2l**, **2m**, **2n**, **2o, 2p**, **2q**, **2r**, **2s**, **2t, 2x**, **2y**, and **2z** were commercially available. **2e**[17] and **2f**[18] were reported in the literature.

2a ^{1}H NMR (400 MHz, C_4D_8O): 7.90 (2H, d, *J* = 8.4 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 3.77 (3H, s).
^{13}C NMR (100 MHz, C_4D_8O): 166.5, 163.4, 131.5, 123.3, 113.3, 54.7.

2b ^{1}H NMR (400 MHz, CD_3OD): 7.93 (2H, d, *J* = 8.8 Hz), 7.48 (2H, d, *J* = 8.4 Hz), 1.33 (9H, s).
^{13}C NMR (100 MHz, CD_3OD): 167.7, 157.6, 130.5, 128.9, 126.3, 35.9, 31.5.

2c ^{1}H NMR (400 MHz, C_4D_8O):8.03 (2H, d, *J* = 8.0 Hz), 7.66 (2H, d, *J* = 8.0 Hz), 7.62 (2H, d, *J* = 7.6 Hz), 7.38 (2H, t, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.6 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 166.3, 145.0, 139.9, 130.0, 129.7, 128.6, 127.8, 126.9, 126.5.

2d ^{1}H NMR (400 MHz, C_4D_8O): 7.91 (2H, d, *J* = 8.4 Hz), 7.44 (2H, d, *J* = 8.0 Hz), 6.72 (1H, dd, *J* = 17.6, 6.8 Hz), 5.84 (1H, dd, *J* = 18.0, 0.8 Hz), 5.27 (1H, dd, *J* = 11.2, 0.8 Hz).

^{13}C NMR (100 MHz, C_4D_8O): 166.2, 141.5, 136.1, 130.1, 129.7, 125.8, 115.3.

2e ^{1}H NMR (400 MHz, C_4D_8O): 7.92 (2H, d, *J* = 7.2 Hz), 7.44 (2H, d, *J* = 7.6 Hz), 4.24 (2H, s), 3.32 (3H, s).
^{13}C NMR (100 MHz, C_4D_8O): 166.0, 131.3, 130.7, 129.6, 127.1, 88.2, 85.1, 59.7, 56.7.

2f ^{1}H NMR (400 MHz, C_4D_8O): 7.92 (2H, d, *J* = 7.6 Hz), 7.29 (2H, d, *J* = 7.6 Hz), 3.82 (1H, s), 3.03 (1H, t, *J* = 5.2 Hz), 2.66 (1H, d, *J* = 5.6 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 166.3, 143.2, 130.5, 129.6, 125.1, 51.2, 50.7.

2g ^{1}H NMR (400 MHz, C_4D_8O): 10.0 (1H, s), 8.12 (2H, d, *J* = 8.0 Hz), 7.91 (2H, d, *J* = 8.8 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 190.8, 165.7, 139.5, 135.5, 130.0, 128.9.

2h ^{1}H NMR (400 MHz, C_4D_8O): 8.08 (2H, d, *J* = 8.4 Hz), 7.78 (2H, d, *J* = 8.4 Hz), 7.74 (2H, d, *J* = 7.2 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.45 (2H, d, *J* = 7.6 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 194.3, 165.9, 141.1, 137.2, 133.9, 132.3, 129.7, 129.3, 129.3, 128.2.

2i ^{1}H NMR (400 MHz, C_4D_8O): 8.02 (2H, d, *J* = 8.4 Hz), 8.03 (2H, d, *J* = 8.4 Hz), 3.84 (3H, s).
^{13}C NMR (100 MHz, C_4D_8O): 165.8, 165.3, 134.7, 133.7, 129.4, 129.1, 51.5.

2j ^{1}H NMR (400 MHz, C_4D_8O): 8.07 (2H, d, *J* = 8.4 Hz), 7.77 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 165.2, 134.6, 132.0, 130.0, 117.5, 116.2.

2k ^{1}H NMR (400 MHz, C_4D_8O): 8.00 (2H, dd, *J* = 8.8, 5.6 Hz), 7.11 (2H, t, *J* = 8.8 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 165.8, 165.6 (d, $J_{(C\text{-}F)}$= 252.7 Hz), 132.2 (d, $J_{(C\text{-}CCF)}$ = 9.1 Hz), 127.5, 115.6 (d, $J_{(C\text{-}CF)}$ = 22.2 Hz).

2l ^{1}H NMR (300 MHz, CD_3OD): 7.98 (2H, d, *J* = 8.7 Hz), 7.46 (2H, d, *J* = 8.7 Hz).
^{13}C NMR (75 MHz, CD_3OD): 168.7, 140.3, 132.3, 130.8, 129.8

2m ^{1}H NMR (400 MHz, C_4D_8O): 7.85 (2H, d, *J* = 8.4 Hz), 7.57 (2H, d, *J* = 8.8 Hz)
^{13}C NMR (100 MHz, C_4D_8O): 165.9, 131.5, 131.3, 130.1, 127.2.

2n ^{1}H NMR (400 MHz, C_4D_8O): 7.78 (2H, d, *J* = 8.4 Hz), 7.69 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 166.0, 137.5, 131.0, 130.5, 99.9, .

2o ^{1}H NMR (400 MHz, C_4D_8O): 8.18 (2H, d, *J* = 8.4 Hz), 7.78 (2H, d, *J* = 8.4 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 167.8, 135.0 (q, $J_{(C\text{-}CF)}$ = 32.1 Hz), 131.2, 126.3 (q, $J_{(C\text{-}CCF)}$ = 3.3 Hz), 125.1 (q, $^{1}J_{(C\text{-}F)}$ = 271.9 Hz), 123.7.

2p ^{1}H NMR (400 MHz, C_4D_8O): 8.73 (1H, s), 8.38 (1H, d, *J* = 8.4 Hz), 8.31 (1H, d, *J* = 7.6 Hz), 7.68 (1H, dd, *J* = 8.0, 7.6 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 164.7, 148.3, 135.0, 132.6, 129.6, 126.8, 124.0

2q ^{1}H NMR (400 MHz, CD_3OD): 6.85 (2H, s), 2.28 (6H, s), 2.24 (3H, s).
^{13}C NMR (100 MHz): 173.8, 134.0, 135.3, 133.2, 129.0, 21.2, 19.9.

2r ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (2H, d, *J* = 8.8 Hz), 6.63 (2H, d, *J* = 8.4 Hz), 3.85 (3H, s), 3.03 (6H, s).
^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 153.1, 131.1, 116.8, 110.6, 51.5, 40.1.

2s ^{1}H NMR (400 MHz, CD_3OD): 7.71 (1H, s), 7.19 (1H, d, *J* = 3.2 Hz), 6.58 (1H, d, *J* = 1.6 Hz).
^{13}C NMR (100 MHz, CD_3OD): 161.9, 148.0, 146.5, 118.9, 112.9.

2t ^{1}H NMR (400 MHz, CD_3OD): 7.76 (1H, d, *J* = 3.6 Hz), 7.69 (1H, d, *J* = 4.8 Hz), 7.12 (1H, dd, *J* = 4.8, 4.0 Hz).
^{13}C NMR (100 MHz, CD_3OD): 165.3, 135.7, 134.6, 133.8, 128.9.

2u ^{1}H NMR (400 MHz, CD_3OD): 7.93 (1H, d, *J* = 8.8 Hz), 7.77 (1H, s), 7.48 (1H, d, *J* = 8.8 Hz), 7.06 (1H, s), 1.60 (9H, s).
^{13}C NMR (100 MHz, CD_3OD): 164.6, 150.3, 137.6, 134.0, 130.7, 130.4, 125.8, 117.4, 117.1, 113.8, 86.3, 27.9.
Anal. Calcd. For $C_{14}H_{14}BrNO_4$: C 49.43, H 4.15. Found: C 49.39, H 4.22.

2v ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (2H, d, *J* = 8.0 Hz), 7.45 (2H, d, *J* = 8.4 Hz), 4.74 (1H, t, *J* = 6.0 Hz), 3.69 (1H, dd, *J* = 10, 6.4 Hz), 3.52 (1H, dd, *J* = 10, 5.6 Hz), 0.87 (9H, s), 0.83 (9H, s), 0.06 (3H, s), -0.06 (3H, s), -0.07 (3H, s), -0.09 (3H, s).
^{13}C NMR (100 MHz, $CDCl_3$): 172.2, 149.2, 129.9, 128.2, 126.6, 75.6, 69.5, 25.9, 25.8, 18.4, 18.3, -4.8, -4.8, -5.5, -5.6.
Anal. Calcd. For $C_{21}H_{38}O_4Si_2$: C 61.41, H 9.33. Found: C 61.62, H 9.24.

2w ^{1}H NMR (400 MHz, C_4D_8O): 7.93 (2H, d, *J* = 8.4 Hz), 7.39 (2H, d, *J* = 8.0 Hz), 5.35 (1H,t, *J* =

6.8 Hz), 4.25 (1H, dd, *J* = 8.4, 6.8 Hz), 3.53 (1H, t, *J* = 8.0 Hz), 1.42 (3H, s), 1.36 (3H, s).
^{13}C NMR (100 MHz, C_4D_8O): 166.5, 145.0, 130.4, 129.7, 125.7, 109.6, 77.4, 71.3, 25.9.25.2.
Anal. Calcd. For $C_{12}H_{14}O_4$: C 64.85, H 6.35. Found: C 64.56, H 6.53.

2x ^{1}H NMR (400 MHz, CD_3OD): 7.66 (1H, d, *J* = 16.0 Hz), 7.37-58 (5H, m), 6.46 (1H, d, *J* = 16.0 Hz).
^{13}C NMR (100 MHz, CD_3OD): 170.3, 146.3, 135.8, 131.4, 130.0, 129.2, 119.3.

2y ^{1}H NMR (400 MHz, C_4D_8O): 7.53 (1H, d, *J* = 16.4 Hz), 7.48-50 (4H, m), 6.44 (1H, d, *J* = 16.0 Hz).
^{13}C NMR (100 MHz, C_4D_8O): 166.5, 142.5, 134.0, 131.8, 129.5, 123.7, 119.6.

2z ^{1}H NMR (400 MHz, C_4D_8O): 7.52 (1H, d, *J* = 16.8 Hz), 7.47 (2H, d, *J* = 8.8 Hz), 6.87 (2H, d, *J* = 8.8 Hz), 6.26 (1H, d, *J* = 16.4 Hz), 3.75 (3H, s).
^{13}C NMR (100 MHz, C_4D_8O): 167.1, 161.5, 143.8, 129.5, 127.5, 116.1, 114.1, 54.6.

Stoichiometric reaction of (IPr)Cu-complex

[(IPr)Cu(O*t*Bu)] was prepared according to the literatures, [19] using *t*BuOK instead of *t*BuONa.
^{1}H NMR (400 MHz, CD_2Cl_2): 7.50 (2H, t, *J* = 8.0 Hz), 7.32 (4H, d, *J* = 8.0 Hz), 7.12 (2H, s), 2.61 (4H, sept, *J* = 6.8 Hz), 1.32 (12H, d, *J* = 6.8 Hz), 1.21 (12H, d, *J* = 6.8 Hz), 0.72 (9H, s).
^{13}C NMR (100 MHz, CD_2Cl_2): 182.8, 146.1, 135.5, 130.4, 124.3, 123.2, 68.4, 36.3, 29.0, 24.7, 24.2.

Synthesis of [(IPr)CuC$_6$H$_4$-4-OMe] (3)

1a (200 mg, 0.91 mmol) was added to a stirred solution of [(IPr)Cu(O*t*Bu)] (482 mg, 0.91 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 1 h, and then THF was removed under reduced pressure. The resulting white solid was washed by hexane, dried under reduced pressure, and recrystallized in THF/toluene to give the corresponding [(IPr)CuC$_6$H$_4$-4-OMe] complex **3** (470 mg) in 91% yield.
^{1}H NMR (400 MHz, CD_2Cl_2): 7.52 (2H, t, *J* = 7.6 Hz), 7.35 (4H, d, *J* = 7.6 Hz), 7.18 (2H, s), 6.98 (2H, d, *J* = 8.4 Hz), 6.46 (2H, d, *J* = 8.4 Hz), 2.69 (4H, sept, *J* = 6.8 Hz), 1.37 (12H, d, *J* = 6.8 Hz), 1.28 (12H, d, *J* = 7.2 Hz).
^{13}C NMR (100 MHz, CD_2Cl_2): 185.0, 157.2, 155.9, 146.3, 140.7, 135.4, 130.4, 124.3, 123.1, 112.0, 54.9, 29.1, 25.0, 23.8
Anal. Calcd. For $C_{34}H_{43}CuN_2O$: C 73.02, H 7.75. Found: C 72.81, H 7.74.

Synthesis of [(IPr)CuOCOC$_6$H$_4$-4-OMe] (4)

CO_2 was introduced to a stirred solution of **3** (762 mg, 1.36 mmol) in THF (10 mL) at -78 ˚C. The reaction mixture was stirred for 10 min, allowed to warm to room temperature, and then stirred an additional 10 min. THF was removed under reduced pressure. The resulting white solid was recrystallized in THF/toluene to give the corresponding [(IPr)CuOCOC$_6$H$_4$-4-OMe] complex **4** (756 mg) in 92% yield.

^{1}H NMR (400 MHz, CD_2Cl_2): 7.71 (2H, d, *J* = 8.8 Hz), 7.55 (2H, t, *J* = 8.0 Hz), 7.37 (4H, d, *J* = 8.0 Hz), 7.21 (2H, s), 6.72 (2H, d, *J* = 8.8 Hz), 2.64 (4H, sept, *J* = 6.8 Hz), 1.35 (12H, d, *J* = 6.8 Hz), 1.25 (12H, d, *J* = 7.2 Hz).
^{13}C NMR (100 MHz, CD_2Cl_2): 1808, 171.7, 161.6, 146.2, 135.1, 131.5, 130.7, 123.1, 124.5, 123.8, 112.8.
Anal. Calcd. For $C_{35}H_{43}CuN_2O_3$: C 69.68, H 7.18. Found: C 69.58, H 7.17.

X-ray Crystallographic Analysis. A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at –100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ= 0.71069 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinements were performed on F^2 anisotropically for non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. THF molecules in **3**, **4** were refined isotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance.

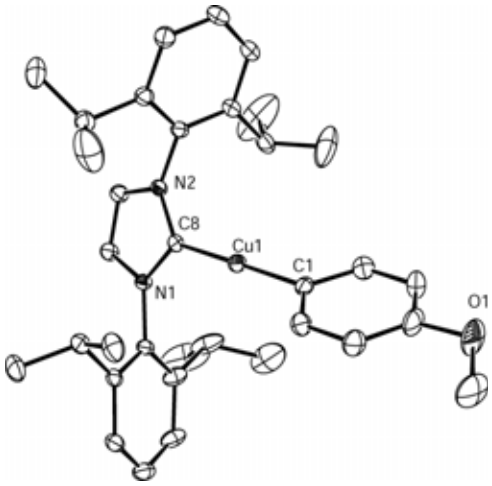

Figure S1. ORTEP structure of **3** (thermal ellipsoids at 50% level; hydrogen atom are omitted for clarity).

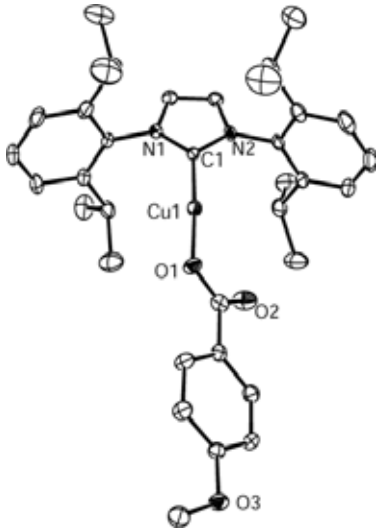

Figure S2. ORTEP structure of **4** (thermal ellipsoids at 50% level; hydrogen atom are omitted for clarity).

References

1) A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523-14534.

2) V. Jurkauskas, J. P. Sadighi, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 2417-2420.

3) K. Ukai, M. Aoki, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc*. **2006**, *128*, 8706-8707.

4) B. Carlson, G. D. Phelan, W. Kaminsky, L. Dalton, X. Jiang, S. Liu, A. K. Y. Jen, *J. Am. Chem. Soc*. **2002**, *124*, 14162-14172.

5) S. Ueno, N. Chatani, F. Kakiuchi, *J. Am. Chem. Soc*. **2007**, *129*, 6098-6099.

6) Y. Kitaura, A. Sakurai, T. Udzu, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron* **2007**, *63*,

10596-10602.

7) M. Tobisu, Y. Kita, N. Chatani, *J. Am. Chem. Soc*. **2006**, *128*, 8152-8153.

8) D. V. Gribkov, S. J. Pastine, M. Schnürch, D. Sames, *J. Am. Chem. Soc*. **2007**, *129*, 11750-11755.

9) R. Shintani, K. Takatsu, T. Hayashi, *Angew. Chem.* **2007**, *119*, 3809-3811; *Angew. Chem. Int. Ed*. **2007**, *46*, 3735-3737.

10) R. A. Bowie, O. C. Musgrave, *J. Chem. Soc*. C, **1966**, 566-571.

11) A. L. S. Thompson, G. W. Kabalka, M. R. Akula, J. W. Huffman, *Synthesis* **2005**, 547-550.

12) H. Chaumeil, S. Signorella, C. LeDrian, *Tetrahedron* **2000**, *56*, 9655-9662.

13) H. C.Brown, T. E. Cole, *Organometallics* **1983**, *2*, 1316-1319.

14) S. T. Jan, K. Li, S. Vig, A. Rudolph, F. M. Uckun, *Tetrahedron Lett.* **1999**, *40*, 193-196.

15) L. Dias, P. R. R. Meira, *J. Org. Chem.* **2005**, *70*, 4762-4773.

16) H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc*. **1975**, *97*, 5249-5255.

17) S. Nakatani, M. Ikura, S. Yamamoto, Y. Nishita, S. Itadani, H. Habashita, T. Sugiura, K. Ogawa, H. Ohno, K. Takahashi, H. Nakai, M. Toda, *Bioorg. Med. Chem*. **2006**, *14*, 5402-5422.

18) B. S. Lane, M. Vogt, V. J. DeRose, K. Burgess, *J. Am. Chem. Soc*. **2002**, *124*, 11946-11954.

19) N. P. Mankad, D. S. Laitar, J. P. Sadighi, *Organometallics* **2004**, *23*, 3369-3371.

Reference [1a] is as follows: H. Arakawa, M. Aresta, J. N. Armor, N. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, D. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev*. **2001,** *101*, 953-996.