REFERENCES AND NOTES

1. D. E. Fowler, in *Encyclopedia of Materials Characterization*, C. R. Brundle, C. A. Evans, Jr., S. Wilson, Eds. (Butterworth-Heinemann, Boston, 1992), pp. 723–735.
2. G. Schütz *et al.*, *Phys. Rev. Lett.* **58**, 737 (1987); G. Schütz *et al.*, *Z. Phys. B* **73**, 67 (1988); G. Schütz *et al.*, *ibid.* **75**, 495 (1989).
3. C. T. Chen, F. Sette, Y. Ma, S. Modesti, *Phys. Rev. B* **42**, 7262 (1990).
4. F. Sette, C. T. Chen, Y. Ma, S. Modesti, N. V. Smith, in *X-Ray Absorption Fine Structure*, S. S. Hasnain, Ed. (Ellis Horwood, Chichester, United Kingdom, 1991), pp. 96–105.
5. B. P. Tonner and G. R. Harp, *Rev. Sci. Instrum.* **59**, 853 (1988); ______, S. F. Koranda, J. Zhang, *ibid.* **63**, 564 (1992).
6. The diffraction limit can be overcome by near-field optical techniques, as discussed by: D. W. Pohl, in *Advances in Optical and Electron Microscopy*, C. J. R. Sheppard and T. Mulvey, Eds. (Academic Press, London, 1990), pp. 243–312; E. Betzig and J. K. Trautman, *Science* **257**, 189 (1992).
7. E. Bauer, in *Chemistry and Physics of Solid Surfaces VIII*, R. Vanselow and R. Howe, Eds. (Springer, Berlin, 1990), pp. 264–287; R. M. Tromp and M. C. Reuter, *Ultramicroscopy* **36**, 99 (1991).
8. K. J. Kim, *SPIE* **1345**, 116 (1990).
9. J. Stöhr, *NEXAFS Spectroscopy* (Springer Series in Surface Sciences 25, Springer, Heidelberg, 1992).
10. B. P. Tonner, *Nucl. Instrum. Methods Phys. Res. A* **291**, 60 (1990).
11. For a review, see *X-Ray Microscopy II*, D. Sayre, M. Howells, J. Kirz, H. Rarback, Eds. (Springer Series in Optical Sciences 56, Springer, Heidelberg, 1988); J. Voss *et al.*, *J. X-ray Sci. Technol.* **3**, 85 (1992).
12. Advanced Light Source Handbook (PUB-643 Rev. 2, Lawrence Berkeley Laboratory, University of California, April 1989) (unpublished).
13. B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972), chap. 9; M. Hartmann, *J. Magn. Magn. Mater.* **68**, 298 (1987).
14. W. Rave, R. Schäfer, A. Hubert, *J. Magn. Magn. Mater.* **65**, 7 (1987).
15. J. N. Chapman, *J. Phys. D.* **17**, 623 (1984).
16. M. R. Scheinfein, J. Unguris, M. H. Kelley, D. T. Pierce, R. J. Celotta, *Rev. Sci. Instrum.* **61**, 2501 (1990).
17. M. S. Altman *et al.*, *Mater. Res. Soc. Symp. Proc.* **232**, 125 (1991).
18. D. Rugar *et al.*, *J. Appl. Phys.* **68**, 1169 (1990).

19. We are grateful to G. Castro for initiating the photoelectron microscopy effort at IBM Almaden; S. Lambert for writing the bit pattern on the disk; and D. Pierce, H. Poppa, R. Browning, and I. McFadyen for helpful discussions. The work was carried out in part at SSRL, which is operated by the Department of Energy, Division of Chemical Sciences.

23 September 1992; accepted 25 November 1992

Reaction of a Tantalum Alkylidene Complex with Dinuclear Metal Carbonyls: Formation of C_3 Ligands

Grant Proulx and Robert G. Bergman*

The mechanisms of reactions that deoxygenate carbon monoxide (CO) and convert it into longer chain hydrocarbons are not well understood. A series of reactions between "early" and "late" transition metal complexes that result in CO coupling reactions in a homogeneous solution are reported. In one example, the Schrock tantalum-methylene complex (η^5-C_5H_5)$_2$Ta(CH_2)(CH_3) reacts with the dinuclear metal carbonyls $Co_2(CO)_8$ and $Fe_2(CO)_9$ in a novel fashion to yield a $C_3H_2O_2$ ligand bridging three metal centers. Reaction of the tantalum-methylene complex with $Re_2(CO)_{10}$ leads to an even more substantial change in which extensive rearrangement along with three-carbon coupling occurs. An oxygen atom is removed from one CO group, leading to the novel oxotantalum compound (η^5-C_5H_5)$_2$(CH_3)Ta=O. Simultaneously, the carbon atom from the transformed CO couples with two CH_2 groups initially bound to tantalum and the CH_2 hydrogens are rearranged to produce a CH_3–CC ligand. Low-temperature nuclear magnetic resonance and isotope tracer experiments have provided preliminary information about the mechanisms of these unusual carbon-carbon bond-forming reactions.

Carbon monoxide (CO) is an important potential building block in chemical synthesis (*1*). "Synthesis gas," a mixture of CO and H_2, is used in metal surface-catalyzed chemical transformations, such as the Fischer-Tropsch process, that lead to longer chain organic molecules. These reactions have been studied by ultrahigh vacuum (UHV) techniques, and surface-bound carbide, CH, and CH_2 fragments have been implicated as intermediates (*1, 2*). However, their mechanisms are still not well understood. A few analogous homogeneous solution reactions are known in which CO molecules are coupled (*3–6*) or cleaved (*7, 8*), but more extensive homogeneous C–C bond-forming processes with this ligand are still rare. Examples of CO oligomerization processes that occur in a homogeneous solution would provide an opportunity for detailed study of this fundamental transformation.

We report the reaction between the first "early" (left side of the periodic table) transition metal (alkyl) (methylene) complex, prepared by Schrock in 1975 (*9*), and three "late" (right side) dinuclear metal carbonyls: $Co_2(CO)_8$, $Fe_2(CO)_9$, and $Re_2(CO)_{10}$. In spite of the superficial similarity of the carbonyls, the reaction proceeds similarly in two of these cases but takes a dramatically different course in the third. With Co and Fe, two CO ligands and a CH_2 fragment directly couple with one another. In the Re system, a number of substantial changes take place: hydrogens are rearranged in two CH_2 groups to give a carbon atom and a methyl group; an oxygen atom is removed from a CO ligand and transferred to a second tantalum moiety [generating the novel complex $Cp_2(CH_3)$Ta=O (Cp = η^5-C_5H_5)]; and the resulting carbon fragments are coupled to give a coordinated C_3 (methylacetylide) ligand.

Treatment of 1 eq (equivalent) of $Cp_2Ta(CH_2)(CH_3)$ (**1**) with 1 eq of $Co_2(CO)_8$ or $Fe_2(CO)_9$ above −30°C for 3 hours resulted in >90% [^{1}H nuclear magnetic resonance (NMR)] yields of dark brown and dark red compounds, respectively, with the stoichiometries $Cp_2Ta(CH_3)(C_3H_2O_2)Co_2(CO)_6$ (**2**) and $Cp_2Ta(CH_3)(C_3H_2O_2)Fe_2(CO)_7$ (**3**). Compound **2** was isolated in 49% yield and compound **3** in 47% yield by benzene-pentane recrystallization. The ^{1}H NMR spectra (*10, 11*) of **2** and **3** are similar, with two doublets attributable to two coupled inequivalent CH_2 protons. The ^{13}C NMR spectra (*10, 11*) of **2** and **3** are also quite similar with resonances attributable to an allylic CH_2 and a Ta–CH_3 ligand. The spectroscopic data eliminate structures for these compounds that retain the CH_2 ligand on the Ta center and suggest attack of this group on a CO ligand.

To confirm this inference, the x-ray structures of **2** and **3** were determined. The molecular geometries are shown in Fig. 1, A and B. These show heterotrinuclear structures in which a ($C_3H_2O_2$) unit, formed from the direct coupling of two CO ligands and the carbene C atom, bridges the three metal centers and is bound to the Ta through two O atoms. One late metal center is associated in an allylic fashion with all three carbons of the ligand, and the second late metal center is bound to only a single C atom of this ligand (*12, 13*).

In contrast to the above results, treatment of 2 eq of **1** with 1 eq of the larger *5d* metal carbonyl $Re_2(CO)_{10}$ for 1 hour above 5°C resulted in the formation of a deep red compound in 62% isolated yield [based on $Re_2(CO)_{10}$] with the stoichiometry $Cp_2Ta(C_3H_3)Re_2(CO)_9$ (**4**). Overall, formation of **4** requires a net loss of H_2O from **1** and the metal carbonyl. However, free H_2O was not produced in this reaction; instead, $Cp_2Ta(O)(CH_3)$ (**5**) (*14, 15*) and CH_4 were formed. Control experiments demonstrated that treatment of **1** with

---

Department of Chemistry, University of California, Berkeley, CA 94720.

*To whom correspondence should be addressed.

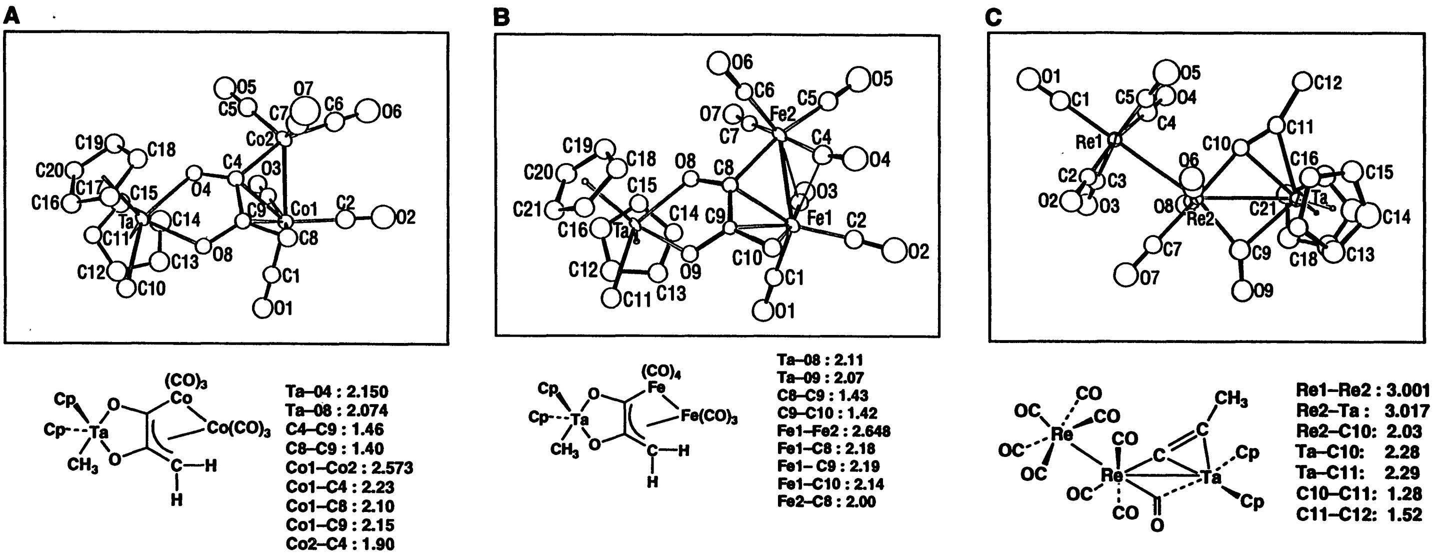

Fig. 1. Line drawing, ORTEP diagram, and selected bond distances for the molecular structure of (**A**) $Cp_2Ta(CH_3)(C_3H_2O_2)Co_2(CO)_6$ (**2**); (**B**) $Cp_2Ta(CH_3)(C_3H_2O_2)Fe_2(CO)_7$ (**3**); and (**C**) $Cp_2Ta(C_3H_3)Re_2(CO)_9$ (**4**).

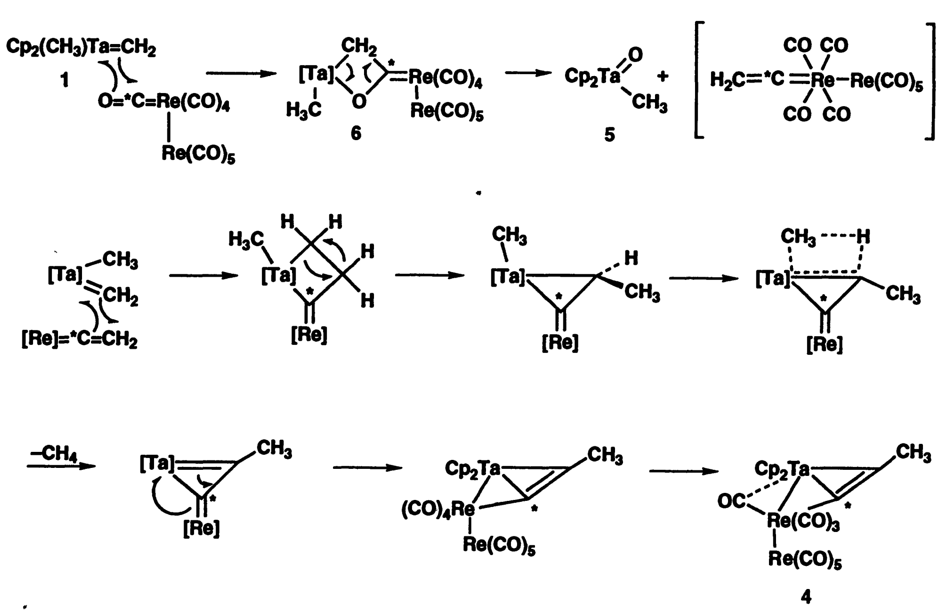

Fig. 2. Suggested mechanism for the formation of $Cp_2Ta(C_3H_3)Re_2(CO)_9$ (**4**). The asterisk indicates the fate of one ^{13}C atom initially bound to $Re_2(^{13}CO)_{10}$.

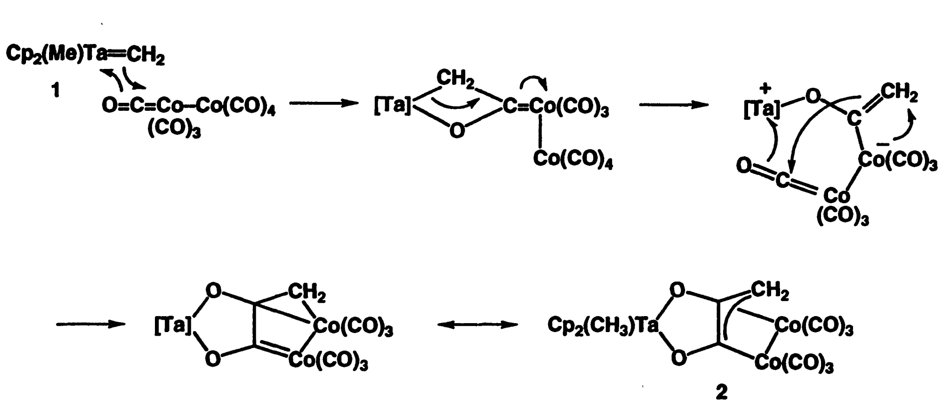

Fig. 3. Suggested mechanism for the formation of $Cp_2Ta(CH_3)(C_3H_2O_2)Co_2(CO)_6$ (**2**). Note that in several of the structures, dative (donor-acceptor) metal-metal bonds are required to establish closed shell (18-electron) configurations at the metal centers.

varying amounts of H_2O does not form **5**. The ^{13}C NMR spectrum (*16*) of **4** shows resonances attributable to three different types of C atoms, other than those associated with CO and Cp ligands. In the ^{13}C spectrum an unusually downfield resonance was observed [tetrahydrofuran (THF)-d_8] at δ 266.53 attributable to a CO ligand. Similarly, the infrared spectrum of **4** exhibits a stretch due to ν(CO) at 1713 cm^{-1}. Once again, x-ray diffraction was required to conclusively establish the structure of the product. The molecular geometry (Fig. 1C) reveals a trinuclear structure in which two metal centers are bridged by both a CO molecule and a three-carbon methylacetylide ligand. Interestingly, this structure verifies a rare example of a bridging CO attached to Ta.

We have carried out initial mechanistic studies on the Re reaction because it appears to be the most unusual of the three processes reported here. In one experiment, the progress of the reaction of **1** with $Re_2(CO)_{10}$ was monitored by variable-temperature NMR. The reactants were mixed at −50°C. Slow warming of the reaction solution showed by ^1H NMR the formation of a new material, different from reactants or products, whose spectral characteristics were consistent with its assignment as oxametallacycle **6** (Fig. 2). On reaching 5°C, this compound reacts with a second molecule of **1**, with loss of 1 eq of CH_4 and 1 eq of **5**, to give **4**. Carrying out the reaction of **1** with ^{13}CO-enriched $Re_2(CO)_{10}$ established that the Re-bound C atom of the C_3 ligand in **4** was formed from a CO ligand initially incorporated in $Re_2(CO)_{10}$.

On the basis of these preliminary results, we propose the pathways summarized in Figs. 2 and 3 as working hypotheses for the mechanisms of the reaction of 1 with $Co_2(CO)_8$, $Fe_2(CO)_9$, and $Re_2(CO)_{10}$. We believe both reactions are initiated by an overall cycloaddition between the $Ta{=}CH_2$ group of 1 and a CO ligand of the dinuclear metal carbonyl complex. After this step, the pathways apparently diverge, as suggested in Figs. 2 and 3. The Re reaction appears to be a Wittig-type interaction between a CO ligand and a $M{=}CH_2$ group in which the carbon and oxygen atoms are simply interchanged to form a vinylidene ligand.

Our experiments record new examples of reactions in homogeneous solution between early and late transition metal complexes. These processes result in overall transformations in which CO molecules are coupled to one another and to CH_2 ligands, in one case with cleavage of the CO bond and accompanying rearrangement of hydrogen on the CH_2 groups. The rapid occurrence of these reactions appears to be a direct result of the interaction of two metal complexes in which the metal centers have very different electronic properties. It is not yet known whether transformations exhibiting related types of cleavage and rearrangement on surfaces (such as the Fischer-Tropsch process which forms alcohols, ketones, or aldehydes from CO and H_2) proceed by mechanisms similar to those involved in the reactions described here. However, the potential analogies are interesting. We hope that our results stimulate further studies of chemical interactions between early and late transition metal carbon-containing species in both homogeneous and heterogeneous media so that the similarities and differences between processes occurring under these two conditions may be better understood.

REFERENCES AND NOTES

1. M. van der Reit, D. Copperthwaite, R. Hunter, G. J. Hutchings, *J. Chem. Soc. Chem. Commun.* **1988**, 512 (1988).
2. G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, Ithaca, NY, 1981).
3. J. E. Bercaw, R. D. Sanner, D. R. McAlister, J. M. Manriquez, *J. Am. Chem. Soc.* **100**, 2716 (1978).
4. C. D. Wood and R. R. Schrock, *ibid.* **101**, 5421 (1979).
5. E. M. Carnahan and S. J. Lippard, *ibid.* **114**, 4166 (1992), and references cited there.
6. R. V. Anslyn, B. D. Santarsiero, R. H. Grubbs, *Organometallics* **7**, 2137 (1988).
7. D. R. Neithamer *et al.*, *J. Am. Chem. Soc.* **111**, 9056 (1989).
8. R. Toreki, R. E. LaPointe, P. T. Wolczanski, *ibid.* **109**, 7558 (1987).
9. R. R. Schrock, *ibid.* **97**, 6577 (1975).
10. Nuclear magnetic resonance (NMR) data for $Cp_2(CH_3)Ta(C_3H_2O_2)Fe_2(CO)_7$ (**3**): ^1H NMR (THF-d_8): δ 6.12 (5H, s, Cp); 6.11 (5H, s, Cp); 2.55 (1H, d, J = 5.2, CH_2); 1.63 (1H, d, J = 5.2, CH_2); and 0.85 (1H, s, CH_3). ^{13}C NMR (THF-d_8): δ 214.19 (s, CO); 198.40 (s, CO); 189.30 (s, CO); 144.43 (s, μ-CO); 112.72 (m, Cp); 112.61 (m, Cp); 100.48 (s, μ_2-C_2O_2); 89.20 (s, μ_2-C_2O_2); 39.65 (t, J_{CH} = 157, CH_2); and 36.38 (q, J_{CH} = 128, CH_3).
11. NMR data for $Cp_2(CH_3)Ta(C_3H_2O_2)Co_2(CO)_6$ (**2**): ^1H NMR (C_6D_6): δ 5.23 (5H, s, Cp); 5.09 (5H, s, Cp); 3.12 (1H, d, J = 2.5, CH_2); 2.49 (1H, d, J = 2.6, CH_2); and 0.65 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 208.97 (s); 207.81 (s); 207.64 (s); 204.18 (s); 139.04 (s); 129.04 (s); 112.92 (s); 112.85 (s); 49.18 (s); and 36.75 (s).
12. Phosphine-substituted uranium carbene complexes have been shown to undergo a similar reaction with dinuclear iron carbonyls; compare with J. W. Gilje and R. E. Cramer, *Inorg. Chim. Acta* **139**, 177 (1987).
13. R. E. Cramer, K. T. Higa, S. L. Pruskin, J. W. Gilje, *J. Am. Chem. Soc.* **105**, 6749 (1983).
14. It is unclear whether $Cp_2Ta(O)(CH_3)$ exists as a discrete monomer or as a mixture of linear or cyclic oligomers containing –(–Ta–O–Ta–O–)– bonds. It is apparent in the ^1H NMR spectrum that a sample of $Cp_2Ta(O)(CH_3)$ warmed above room temperature has resonances that broaden before precipitation of an intractable pale yellow powder occurs, characteristic of this kind of polymerization. Also, mass spectral analysis of **6** shows minor peaks at mass-to-charge (*m/z*) values that correspond to a dimeric form with the most intense peaks appearing at an *m/z* value consistent with the monomer.
15. The analogous pentamethylcyclopentadienyl complex has been prepared: L. L. Whinnery, L. M. Henling, J. E. Bercaw, *J. Am. Chem. Soc.* **113**, 7575 (1991).
16. NMR data for $Cp_2Ta(\mu\text{-}C_3H_3)(\mu\text{-}CO)Re_2(CO)_8$ (**4**): ^1H NMR (THF-d_8): δ 5.27 (10H, s, Cp); and 3.01 (3H, s, CH_3). ^{13}C NMR (THF-d_8): δ 266.53 (s, μ-CO); 200.57 (s, CO); 197.65 (s, CO); 197.40 (s, CO); 139.69 (m, $^3J_{CH}$ = 6.0, $^1J_{CC}$ = 101.4, and $^2J_{CC}$ = 5.0, Ta–C–Re); 127.74 (m, $^1J_{CC}$ = 101.4 and $^2J_{CH}$ = 8.0, C–Me); 102.35 (m, $^1J_{CH}$ = 178, $^2J_{CH}$ = 7.0, and $^3J_{CH}$ = 6.0, Cp); and 18.71 (m, J_{CH} = 128.8 and $^2J_{CC}$ = 5.0, CH_3).

17. We are grateful to the National Science Foundation (grant CHE-9113261) for financial support of this work. We thank F. J. Hollander, director of the U.C. Berkeley x-ray diffraction facility (CHEXRAY), for determination of the x-ray structures.

8 September 1992; accepted 17 November 1992

Shock Amorphization of Cristobalite

A. J. Gratz, L. D. DeLoach, T. M. Clough, W. J. Nellis

Shock amorphization of cristobalite is reported and related to shock metamorphism of quartz, both being silicon dioxide polymorphs. Whereas amorphization of quartz takes place over a broad pressure range and is complete only at 35 to 40 gigapascals (350 to 400 kilobars), amorphization of cristobalite was complete (greater than 99.9 percent) by 28 gigapascals with a relatively sharp phase transformation; lower shock pressures up to 23 gigapascals resulted in no significant amorphization. Also, unlike quartz, there was no sign of lamellar amorphization, which is common in shock compression. Cristobalite amorphization should prove a useful indicator of shock pressure and is the first case of pressure amorphization of isochemical polymorphs. The diaplectic glass that is produced has a refractive index and density essentially identical to those of the diaplectic glass made from quartz, which suggests that both polymorphs collapse during shock to similar disordered phases.

Phase and microstructural changes induced by shock compression are of interest both in high-pressure physics and in studies of meteorite impacts. Materials undergoing such changes provide information about the nature of high-pressure phase transformations and about possible deformation mechanisms in minerals. For example, shock transformation and deformation of SiO_2 quartz have been studied extensively (*1–5*). When shocked to pressures of 15 to 40 GPa, the mixed-phase region (*6*), quartz transforms continuously to a disordered phase without evidence of melting (a diaplectic glass), such as flow features and loss of original grain structure. Diaplectic glass in shocked quartz is formed in the solid state in lamellar regions, usually along crystallographic directions (*7, 8*). Completion of the process at high shock pressures causes the formation of an amorphous material. A similar process occurs in the static compression of quartz in a diamond-anvil cell (*9, 10*).

Shock effects observed in various initial forms of SiO_2 in the laboratory might serve as useful indicators of shock-induced effects and pressures in nature. Notably, shock-induced microstructures in quartz can be observed with an optical microscope as planar deformation features (PDFs) and are used extensively to identify shock metamorphism. At the Cretaceous-Tertiary boundary, for example, quartz grains were shown to contain PDFs attributed to shock loading caused by meteorite impact (*11*). In addition, the extent of SiO_2 amorphization is used to estimate shock pressures, with total amorphization assumed to occur between 35 and 40 GPa, based on the quartz results.

Although shock-induced amorphization has now been observed in a variety of crystals (*12–14*), shock experiments have not been done on polymorphs of the same silicate. For SiO_2, for example, it is important to know to what extent observed phase

---

A. J. Gratz and W. J. Nellis, Institute of Geophysics and Planetary Physics and H Division, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550.

L. D. DeLoach, Y Division, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550.

T. M. Clough, Department of Chemistry, Arizona State University, Tempe, AZ 85287.