

peak. Both the splitting constants and spectral shapes show that PFPE is present as an organized assembly. In contrast, the motion of the probe in water-saturated CO<sub>2</sub> (without surfactant) is isotropic.

At CO<sub>2</sub> densities >13 M, the apparent A<sub>N</sub> in the surfactant solution drops to near that in neat CO<sub>2</sub>. Thus, the observed A<sub>N</sub> results predominately from the presence of 4-hydroxy-TEMPO molecules found outside the microemulsion droplets. The shapes of the spectra support this explanation. The lack of a polar environment for 4-hydroxy-TEMPO is a result of the rapid reduction of the nitroxide by reaction with NH<sub>4</sub><sup>+</sup> within the polar microemulsion core. The reduction in dense CO<sub>2</sub> surfactant solutions follows pseudo first-order kinetics with an apparent rate constant, *k*, of 6.8 × 10<sup>-4</sup> s<sup>-1</sup>. For comparison, *k* is equal to 2.0 × 10<sup>-5</sup> s<sup>-1</sup> for solutions of 4-hydroxy-TEMPO in trifluoroacetic acid and ammonium acetate (pH 3.0). The much larger rate constant may be attributed, in part, to a high degree of nitroxide orientation in the restricted environment of the microemulsion core. The strong sensitivity of the reaction rate to CO<sub>2</sub> density is due to the requirement that a water pool be present before significant ionization and subsequent reduction reaction can occur.

Our FTIR, ultraviolet-visible absorbance, fluorescence, and EPR experiments demonstrate the existence of an aqueous domain in CO<sub>2</sub> with a polarity approaching that of bulk water. Thus, not only do PFPE-based microemulsions offer a thermodynamically stable aqueous domain in a CO<sub>2</sub> phase, but they also appear to offer simultaneously a microenvironment that may not alter significantly the conformation of sequestered proteins. By comparing these results with those of previous studies, the successful formation of a microemulsion with PFPE may be attributed to the weak van der Waals forces of the surfactant tail, the strong tendency of the ionic head group to leave CO<sub>2</sub>, the CF<sub>3</sub> branching and the small size of the head group, which favor bending of the interface about water, and the low solubility of the fluoroether tails in water. Given these guidelines, it should be possible to synthesize additional surfactants for environmentally benign applications in dense CO<sub>2</sub>.

## REFERENCES AND NOTES

1. J. M. DeSimone, Z. Guan, C. S. Elsbernd, *Science* **257**, 945 (1992).
2. J. M. DeSimone *et al.*, *ibid.* **265**, 356 (1994).
3. F. A. Adamsky and E. J. Beckman, *Macromolecules* **27**, 312 (1994).
4. D. J. Dixon, R. A. Bodmeier, K. P. Johnston, *AIChE J.* **39**, 127 (1993).
5. P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **368**, 231 (1994).

6. K. A. Consani and R. D. Smith, *J. Supercrit. Fluids* **3**, 51 (1990).
7. A. Iezzi, R. Enick, J. Brady, *ACS Symp. Ser.* **406**, 122 (1989).
8. E. W. Kaler, J. F. Billman, J. Fulton, R. D. Smith, *J. Phys. Chem.* **95**, 458 (1991).
9. D. G. Peck and K. P. Johnston, *ibid.*, p. 9549.
10. G. J. McFann and K. P. Johnston, *ibid.*, p. 4889.
11. T. A. Hoefling, R. M. Enick, E. J. Beckman, *ibid.*, p. 7127.
12. O. A. ElSeoud, A. M. Chinelatto, M. R. Shimizu, *J. Colloid Interface Sci.* **88**, 420 (1982).
13. K. Harrison, J. Goveas, K. P. Johnston, E. A. O'Rear, *Langmuir* **10**, 3536 (1994).
14. A. Chittofrati *et al.*, *Progr. Colloid Polym. Sci.* **79**, 218 (1989).
15. D. A. Newman, T. A. Hoefling, R. R. Beitle, E. J. Beckman, R. M. Enick, *J. Supercrit. Fluids* **6**, 205 (1993).
16. G. Onori and A. Santucci, *J. Phys. Chem.* **97**, 5430 (1993).
17. The microemulsion solutions were prepared in a miniature stainless steel spectroscopic cell (2.8 mm, path length) with CaF<sub>2</sub> windows (10 mm thick) [S. M. Howdle and M. Poliakoff, in *Supercritical Fluids: Fundamentals for Applications*, NATO ASI Series, Applied Sciences 273, E. Kiran and J. M. H. Levelt-Sengers, Eds. (Kluwer Academic, Dordrecht, 1994), pp. 527-540]. The PFPE + D<sub>2</sub>O + CO<sub>2</sub> mixtures were prepared at 31°C in conditions similar to those of the above phase behavior measurements. The IR spectra were recorded on a Nicolet 730 interferometer with a mercury cadmium telluride detector (2 cm<sup>-1</sup> resolution).
18. M. D. Garrison, D. J. Iuliano, S. S. Saavedra, G. A. Truskey, W. M. Reichert, *J. Colloid Interface Sci.* **148**, 415 (1992).

19. R. Wang, S. Sun, E. J. Bekos, F. V. Bright, *Anal. Chem.* **67**, 149 (1995).
20. All experiments were conducted with stirred high-pressure optical cells and equipment described previously [T. A. Betts and F. V. Bright, *Appl. Spectrosc.* **44**, 1196 (1990)]. Excitation was at 360 nm, and excitation and emission band passes were at 8 nm. The PFPE concentration was always 1.4 weight % as in the above phase equilibria measurements. BSA-Ac was added to as a solid to produce a concentration of 100 nM (6.7 μg/ml) based on the volume of the cell. Water was added with a micro-pipette before charging with CO<sub>2</sub>.
21. J. S. Lundgren, M. P. Heitz, F. V. Bright, *Anal. Chem.* **67**, 3775 (1995).
22. This estimate is based on a calibration based on BSA-Ac in liquid water. It should be considered a lower limit as the Ac quantum yield within microemulsions at all values of W<sub>0</sub> is somewhat less than that in liquid water (21).
23. The molar ratio of water to 4-hydroxy-TEMPO was ~1700:1. Spectra were recorded in a high-pressure recirculating cell [T. W. Randolph and C. Carlier, *J. Phys. Chem.* **96**, 5146 (1992)] at a microwave power of 10 mW, modulation frequency of 100 kHz, and a 1.0-G modulation amplitude.
24. We gratefully acknowledge financial support from NSF (K.P.J. and T.W.R.), the U.S. Environmental Protection Agency (K.P.J.), the U.S. Department of Energy (F.V.B.), the Royal Society of Chemistry (S.M.H.), the Separations Research Program at the University of Texas (K.P.J.), and Unilever Research (K.P.J.). We thank A. Chittofrati for supplying the PFPE surfactant.

15 September 1995; accepted 4 December 1995

## Crystal and Molecular Structures of Hexamethyltungsten and Hexamethylrhenium

Valerie Pfennig and Konrad Seppelt\*

The structure of hexamethyltungsten, W(CH<sub>3</sub>)<sub>6</sub>, was determined by x-ray single-crystal diffraction at -163°C. The molecule has a strongly distorted trigonal prismatic structure with C<sub>3v</sub> symmetry. This irregular structure is not a result of intermolecular forces, but rather represents its true molecular structure. A similar structure, which deviates less from the ideal trigonal prismatic structure, was determined for hexamethylrhenium, Re(CH<sub>3</sub>)<sub>6</sub>. Although these structures violate the simplistic models used to predict the geometry of molecules, they are at least in part explainable by the molecular orbital model.

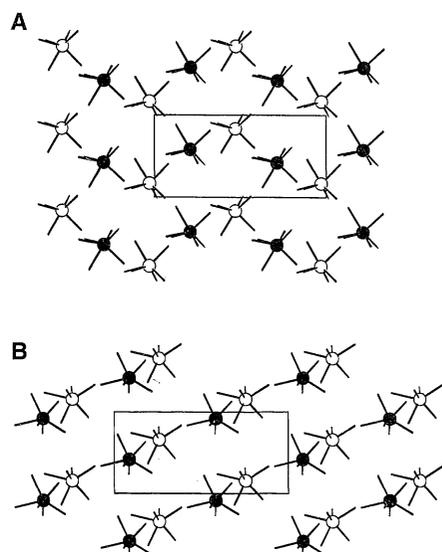
Homoleptic molecules, which have only one kind of ligand surrounding a central atom, are important for checking bond theory against experimental data because structure, stability, and reactivity are not influenced by different ligands. The methyl group is the simplest organic ligand in organometallic chemistry, and permethyl metal derivatives are often surprisingly stable because β eliminations are impossible. However, only three neutral hexamethyl compounds are known to exist: W(CH<sub>3</sub>)<sub>6</sub>, Re(CH<sub>3</sub>)<sub>6</sub>, and Te(CH<sub>3</sub>)<sub>6</sub>. Te(CH<sub>3</sub>)<sub>6</sub> has only recently been prepared (1) and has an octahedral structure (2), as expected.

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany.

\*To whom correspondence should be addressed. E-mail: seppelt@chemie.fu-berlin.de

W(CH<sub>3</sub>)<sub>6</sub> and Re(CH<sub>3</sub>)<sub>6</sub> are unstable compounds that were first synthesized (but not structurally characterized) by Wilkinson and colleagues (3). The finding that isoelectronic Zr(CH<sub>3</sub>)<sub>6</sub><sup>2-</sup> in [Li(CH<sub>3</sub>)<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>Zr(CH<sub>3</sub>)<sub>6</sub><sup>2-</sup> is trigonal prismatic (4) led to increased interest in the structures of hexamethyl compounds, especially because it had been theoretically predicted that certain hexacoordinate d<sup>0</sup> complexes may not be octahedral (5-9). This prediction was supported by the results of a recent gas phase structure determination by electron diffraction, which showed W(CH<sub>3</sub>)<sub>6</sub> to be trigonal prismatic (10).

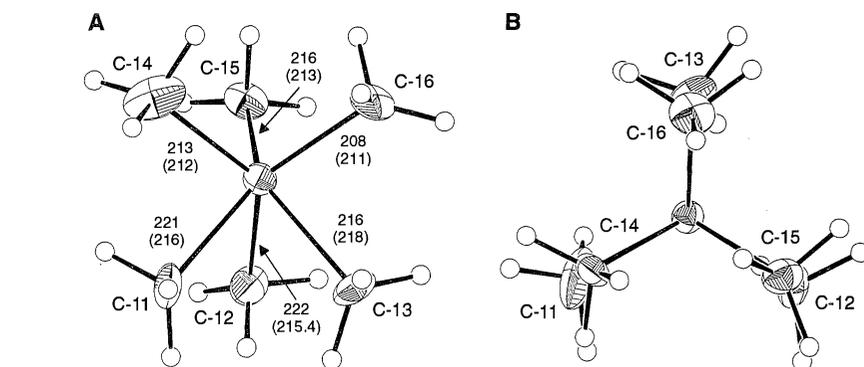
Crystallographically, W(CH<sub>3</sub>)<sub>6</sub> and Re(CH<sub>3</sub>)<sub>6</sub> posed a challenge. The compounds are thermally unstable, even explosive, if pure; Re(CH<sub>3</sub>)<sub>6</sub> is even more sensitive than W(CH<sub>3</sub>)<sub>6</sub>. Moreover, crystals from solutions



**Fig. 1.** (A) Orientation of  $W(CH_3)_6$ -I (●) and  $W(CH_3)_6$ -II (○) in the lattice, shown as a projection into the  $ab$  plane. Both types of molecules form layers that are approximately separated by  $c/4$ . The  $W(CH_3)_6$ -I layer at  $z \approx 1/4$  resembles a nearly square grid, whereas the  $W(CH_3)_6$ -II molecules at  $z \approx 0$  form a nearly hexagonal layer. The diagram also gives an impression of the intermolecular distances within each layer; distances between layers are of similar magnitude. (B) Packing of the  $Re(CH_3)_6$  molecules as projected into the  $ab$  plane. Here, all layers of molecules are nearly hexagonal.

in pentane or isopentane were found to be plastic in character, with very little x-ray diffraction intensity. Only recrystallization from acetone at  $-90^\circ\text{C}$  yielded needle-shaped single crystals for both compounds that diffracted very well at  $-163^\circ\text{C}$  (11).

The unit cell of  $W(CH_3)_6$  contains two crystallographically different molecules, I and II, that are very much alike and differ only in their packing (Fig. 1A). No crystallographic symmetry is enforced on either molecule. We were surprised to find that  $W(CH_3)_6$  does not have the trigonal prismatic ( $D_{3h}$ ) structure, as proposed by the electron diffraction experiment (10); rather, the observed structure can be derived from  $D_{3h}$  by opening up one triplet of methyl groups to C-W-C angles of  $93.3^\circ$  to  $96.9^\circ \pm 0.5^\circ$  and closing the other triplet to C-W-C angles of  $75.4^\circ$  to  $78.2^\circ \pm 0.4^\circ$  (Figs. 2 and 3). The bonds between the latter three methyl groups and tungsten are longer than those between the other three methyl groups and tungsten. The resulting geometry has  $C_{3v}$  symmetry, if small bond length and angle differences between the methyl groups in each triplet are ignored. This molecular shape has one open face, which would be well suited for a weak contact to a neighboring molecule. The shortest nonbonding  $W \cdots C$  contacts found are 458.3, 462.1, 465.0, and 468.6 pm; the corresponding  $W \cdots H$  distances are at best 100 pm less.



**Fig. 2.** Molecular structure of  $W(CH_3)_6$ . (A) View perpendicular to the threefold molecular axis; (B) view down this axis. The thermal ellipsoids are drawn at 50% probability. Bond distances (in picometers) are shown for  $W(CH_3)_6$ -I (upper numbers) and for  $W(CH_3)_6$ -II (lower numbers, in parentheses). Bond angles are as follows [those for  $W(CH_3)_6$ -II are in parentheses]: C-11-W-1-C-12,  $76.7^\circ$  ( $77.9^\circ$ ); C-11-W-1-C-13,  $76.6^\circ$  ( $77.9^\circ$ ); C-12-W-1-C-13,  $75.4^\circ$  ( $78.2^\circ$ ); C-14-W-1-C-15,  $94.9^\circ$  ( $95.8^\circ$ ); C-14-W-1-C-16,  $93.8^\circ$  ( $95.3^\circ$ ); and C-15-W-1-C-16,  $96.9^\circ$  ( $93.3^\circ$ ). Errors are 0.1 pm for all bond distances and  $0.4^\circ$  to  $0.5^\circ$  for all angles.

Neither these nor any of the even longer contacts occupy the open face position; rather, they approach the molecule from the faces perpendicular to the  $C_3$  axis.

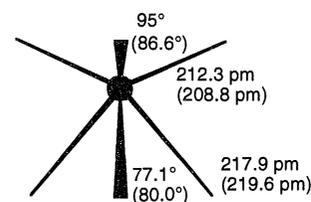
This finding, together with the appearance of two almost identical  $C_{3v}$  structures, leads us to the conclusion that we have determined the true molecular structure of  $W(CH_3)_6$ . This structure would allow a multitude of intramolecular rearrangements in solution or in the gaseous state, such as a movement of the tungsten atom on the threefold axis toward the longer bonded methyl groups, so that the two methyl triplets seem to interchange. The resulting molecule would have the same symmetry, mirrored in a plane perpendicular to the threefold axis. An averaged structure of this nonrigid molecule would have  $D_{3h}$  symmetry, as was found in the gas phase. It remains to be seen whether the electron diffraction data can be fitted to this dynamic  $D_{3h}$  model, or even to a static  $C_{3v}$  model.

For  $Re(CH_3)_6$ , for which no previous structural information is available, we determined a structure less distorted from  $D_{3h}$  symmetry (Figs. 1B, 3, and 4). Again, three methyl groups have shorter bonds and slightly larger angles between each other [ $85.5^\circ$  to  $87.2^\circ \pm 0.6^\circ$ ] than do the other three methyl groups [ $79.5^\circ$  to  $80.4^\circ \pm 0.6^\circ$ ], resulting in a  $C_{3v}$  structure. No crystallographic symmetry or intermolecular forces are imposed on the structure.

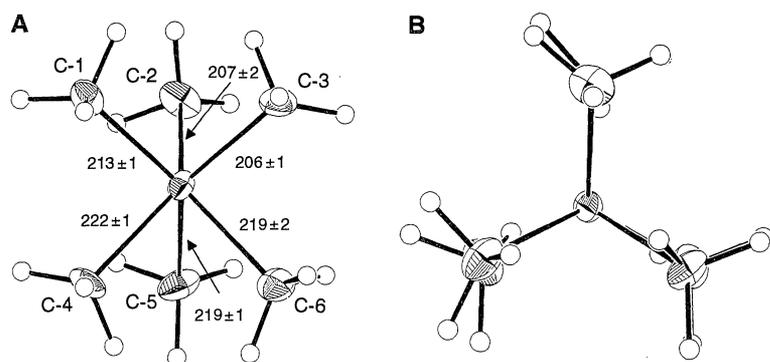
A satisfactory theoretical bond model must explain the observation that the  $d^1$  compound  $Re(CH_3)_6$  is closer to a regular structure than is the  $d^0$  compound  $W(CH_3)_6$ . The valence shell electron pair repulsion model (VSEPR) fails to explain our findings (12). Even a  $D_{3h}$  geometry violates the VSEPR model; the small bond angles on one side of the molecule in the  $C_{3v}$  molecule lead to even greater violations

of this model. The VSEPR model works well widely among main group compounds, as long as coordination numbers of 6 are not exceeded, and it predicts correctly the octahedral geometries of  $WF_6$ ,  $W(OR)_6$ , and  $W(NR_2)_6$  (13). In contrast to  $W(CH_3)_6$ , these ligands contain "nonbonding" electrons, and the bonds between the ligands and tungsten are polarized, with the negative charge located on the ligand. The negative charge on the ligands may explain the success of the VSEPR model in these cases, and its failure for  $W(CH_3)_6$  and  $Re(CH_3)_6$  may even be indicative of an inverted polarity of the bonds. Recently, the VSEPR model was extended by assuming that the core of a  $d^0$  transition metal atom (where all valence electrons have been removed) is no longer spherical, as it is in main group atoms (14). It remains to be seen whether a nonspherical core can be established as a physical reality. In that case, at least a qualitative prediction of the influence of a nonspherical core on the molecular structure would be desirable.

Because nonbonding electrons located at the ligand atoms influence the overall structure greatly, an all electron model is required.



**Fig. 3.** Schematic representation of the  $C_{3v}$  distorted trigonal prism found for  $W(CH_3)_6$  and  $Re(CH_3)_6$ . For illustration of the angles and bond lengths, the  $C_{3v}$  distortion has been exaggerated. Averaged bond lengths (in picometers) and angles are shown for  $W(CH_3)_6$  (upper numbers) and for  $Re(CH_3)_6$  (lower numbers, in parentheses).

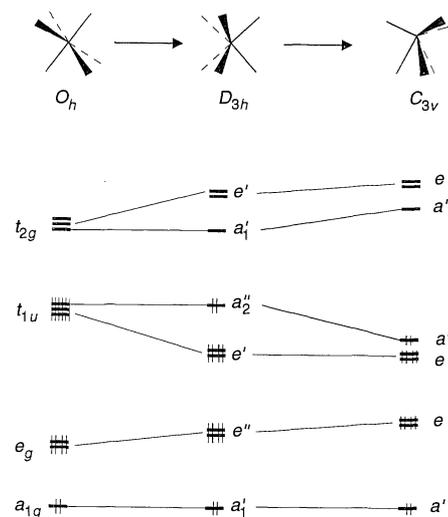


**Fig. 4.** Molecular structure of  $\text{Re}(\text{CH}_3)_6$ . **(A)** View perpendicular to the threefold molecular axis; **(B)** view down this axis. The thermal ellipsoids are drawn at 50% probability. Bond angles are as follows: C-1-Re-C-2,  $85.5^\circ$ ; C-1-Re-C-3,  $87.1^\circ$ ; C-2-Re-C-3,  $87.2^\circ$ ; C-4-Re-C-5,  $80.4^\circ$ ; C-4-Re-C-6,  $79.5^\circ$ ; and C-5-Re-C-6,  $79.7^\circ$ . Errors are  $0.6^\circ$  for all angles.

The valence electron counts for  $\text{W}(\text{CH}_3)_6$  and  $\text{Re}(\text{CH}_3)_6$  are 12 and 13, far from the 18-electron configuration in  $\text{W}(\text{CO})_6$  (or in  $\text{WF}_6$ , where, in addition to the six fully occupied  $\sigma$  molecular orbitals, the  $\pi$  donor character of the F ligands also ensures full occupancy of the  $\pi$  bonding molecular orbitals).  $\text{W}(\text{CH}_3)_6$  and  $\text{Re}(\text{CH}_3)_6$  are thus to be considered as highly electron deficient, leading to a specific, but so far insufficiently investigated, chemistry. An ab initio calculation of the unknown  $\text{WH}_6$  molecule has shown the  $C_{3v}$  type structure to be the global minimum (8, 9). However, the calculated structure of  $\text{WH}_6$  differs in several ways from the structure of  $\text{W}(\text{CH}_3)_6$  determined here: The angles between the ligands of one triplet were predicted to be smaller ( $61^\circ$  to  $62^\circ$ ) than those observed in  $\text{W}(\text{CH}_3)_6$  ( $\sim 75^\circ$ ), and the angles between the ligands of the other triplet were predicted to be larger ( $116^\circ$ ) than those in  $\text{W}(\text{CH}_3)_6$

( $\sim 95^\circ$ ). Moreover, the W-H bonds in the triplet that form the smaller angles are predicted to be shorter, whereas in  $\text{W}(\text{CH}_3)_6$  the corresponding bonds are the longer ones. These discrepancies may be a consequence of the relative sizes of the ligands. A recent ab initio calculation on  $\text{W}(\text{CH}_3)_6$  predicts a regular trigonal prismatic structure (9). Different  $C_{3v}$  deviations were found to have higher energies. It remains to be seen whether more sophisticated calculations, especially in terms of electron correlation, may change this prediction, especially now that experimental data are available.

The qualitative molecular orbital diagram is shown in Fig. 5 (7). With decreasing symmetry, energy is gained for the lower orbitals and lost for the higher orbitals. Therefore, occupation with few electrons should result in the lower symmetry, a complete occupation should result in an  $O_h$  symmetry, and  $D_{3h}$  symmetry should be observed for intermediate occupation. It can then be predicted that the unknown  $\text{Os}(\text{CH}_3)_6$  molecule should have  $D_{3h}$  symmetry, whereas octahedral symmetry should be observed in  $\text{Pt}(\text{CH}_3)_6^{2-}$  (15). Unknown compounds with intermediate electron configuration, such as  $\text{Re}(\text{CH}_3)_6^{2-}$  or  $\text{WF}_2(\text{CH}_3)_4$ , may represent interesting borderline states between  $D_{3h}$  and  $O_h$ . It also seems that the  $C_{3v}$  and  $D_{3h}$  structures are close in energy (5). This may explain why  $\text{Zr}(\text{CH}_3)_6^{2-}$  is  $D_{3h}$  and not  $C_{3v}$ , because the negative charge, located mostly on the ligands, will drive the geometry away from the extremely unfavorable (in terms of ligand repulsion)  $C_{3v}$  geometry. Also, pronounced cation-anion interactions in  $[\text{Li}(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2]_2\text{Zr}(\text{CH}_3)_6$  may account for the  $D_{3h}$  instead of  $C_{3v}$  structure. The electron deficiency of the central atoms in  $\text{W}(\text{CH}_3)_6$  and  $\text{Re}(\text{CH}_3)_6$  may result in intramolecular bridge bonding of the hydrogen atoms, toward the metal atoms (so-called "agostic" hydrogen atoms) or in other structural abnormalities of the methyl groups. Some of



**Fig. 5.** Qualitative molecular orbital diagram for  $d^0 \text{ML}_6$  compounds (where M is the metal and L is the ligand) (7). Occupation of the empty  $a_1'$  orbital in the  $C_{3v}$  structure will drive the structure back to  $D_{3h}$ .

the methyl groups were found to be tilted a few degrees toward the central atom, but no W-C-H angles smaller than  $90^\circ$  were found. However, it is questionable whether the small electron density of the C-H bond can be located precisely enough with the x-ray method in the neighborhood of the heavy central atom to address this question.

## REFERENCES AND NOTES

- L. Ahmed and J. A. Morrison, *J. Am. Chem. Soc.* **112**, 74311 (1990).
- A. Haaland, H. P. Verne, H. V. Volden, J. A. Morrison, *ibid.* **117**, 7554 (1995).
- A. J. Shortland and G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1973**, 872 (1973); A. D. L. Galyer and G. Wilkinson, *ibid.* **1976**, 2235 (1976); K. Mertis and G. Wilkinson, *ibid.*, p. 1488; L. Galyer, K. Mertis, G. Wilkinson, *J. Organomet. Chem.* **85**, C37 (1975).
- P. M. Morse and G. S. Girolami, *J. Am. Chem. Soc.* **111**, 4114 (1989).
- R. Hoffmann, J. M. Howell, A. G. Rossi, *ibid.* **98**, 2484 (1976).
- A. Demolliens, Y. Jean, O. Eisenstein, *Organometallics* **5**, 1457 (1986).
- S. K. Kang, T. A. Albright, O. Eisenstein, *Inorg. Chem.* **28**, 1613 (1989).
- M. Shen, H. F. Schaefer III, H. Partridge, *J. Chem. Phys.* **98**, 508 (1992).
- S. K. Kang, H. Tang, T. A. Albright, *J. Am. Chem. Soc.* **115**, 1971 (1993).
- A. Haaland, A. Hammel, K. Rypdal, H. V. Volden, *ibid.* **112**, 4547 (1990).
- $\text{W}(\text{CH}_3)_6$  crystal parameters: Cell dimensions,  $a = 627.7 \pm 4$  pm,  $b = 1313.5 \pm 4$  pm,  $c = 2083.0 \pm 8$  pm; unit cell volume  $V = 1717 (\pm 1) \times 10^6$  pm $^3$ ; temperature  $T = -163^\circ\text{C}$ ; space group  $Pbc2_1$ , number of molecules in the unit cell  $Z = 8$ , calculated density  $\rho_{\text{calc}} = 2.00$  g/cm $^3$ ; psi scan absorption correction with absorption coefficient  $\mu = 139$  cm $^{-1}$ ;  $\text{MoK}_\alpha$  rays with graphite monochromator; 3824 measured reflections, 3605 unique reflections, 3324 reflections with  $\geq 3\sigma(F)$ , maximal diffraction angle  $\theta_{\text{max}} = 35^\circ$ ; 163 varied parameters; W and C atoms were refined anisotropically, hydrogen isotropically; full least-square matrix refinement, reliability factor  $R = 0.036$ , weighted reliability factor  $R_w = 0.031$ , weighing scheme  $w = 1.5/\sigma^2(F)$ .  $\text{Re}(\text{CH}_3)_6$  crystal parameters: cell dimensions,  $a = 1331.8 \pm 4$  pm,  $b = 626.3 \pm 2$  pm,  $c = 1114.6 \pm 2$  pm;  $\beta = 113.99(1)^\circ$ ;  $V = 849.3 (\pm 4) \times 10^6$  pm $^3$ ;  $T = -163^\circ\text{C}$ ; space group  $C_{2v}$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.16$  g/cm $^3$ ,  $\mu = 142$  cm $^{-1}$ ;  $\text{MoK}_\alpha$  rays with graphite monochromator; 1235 measured reflections, 1196 unique reflections, 1128 reflections with  $\geq 3\sigma(F)$ ,  $\theta_{\text{max}} = 30^\circ$ , 89 varied parameters; Re and C atoms were refined anisotropically, hydrogen isotropically; full least-square matrix refinement,  $R = 0.027$ ,  $R_w = 0.024$ ,  $w = 1/\sigma^2(F) + 0.0001F^2$ . Further details on the crystal structure determinations can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftliche-Technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany (accession number CSD 59174).
- R. J. Gillespie, *Chem. Soc. Rev.* **21**, 59 (1991).
- H. M. Seip and R. Seip, *Acta Chem. Scand.* **20**, 2698 (1966); M. Kimura, V. Schomaker, D. W. Smith, E. Weinstock, *J. Chem. Phys.* **48**, 4001 (1968); A. Haaland, K. Rypdal, H. V. Volden, E. Jacob, J. Weidlein, *Acta Chem. Scand.* **A43**, 911 (1989); K. Hagen, C. J. Holwill, D. A. Rice, J. D. Runnacles, *ibid.* **A42**, 578 (1988).
- R. J. Gillespie, *J. Chem. Educ.* **69**, 116 (1992).
- Vibrational spectra indicate an octahedral symmetry for  $\text{Pt}(\text{CH}_3)_6^{2-}$  [G. W. Rice and R. S. Tobias, *J. Chem. Soc. Chem. Commun.* **1975**, 994; *J. Am. Chem. Soc.* **99**, 2141 (1977); C. S. Crease and J. A. Creighton, *J. Organomet. Chem.* **157**, 243 (1978)].
- Supported by Fonds der Chemischen Industrie.

28 September 1995; accepted 14 November 1995