and the more strongly electrophilic acetyl chloride kinetically attacking the hard ring oxygen. The reactivity observed on treatment with TCNE is somewhat more difficult to rationalize; the possibility that the reductive elimination of ethylene oxide is triggered not by coordination of the olefin but by one-electron oxidation of the metal center is currently under investigation.

Acknowledgment. We thank Dr. William Streib for the X-ray crystal structure determination. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from Union Carbide Corp. is gratefully acknowledged.

Supplementary Material Available: Details of the data collection and structure solution and listings of atomic positional and thermal parameters, complete bond distance and angle data and least-squares planes (12 pages); a listing of F_o vs F_c (6 pages). Ordering information is given on any current masthead page.

C–H Addition Followed by Alkyne Insertion into the Metal–Hydrogen Bond of an Iridium Complex

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Received August 14, 1989

Summary: Thermal C–H activation of benzene is observed with $[Ir(COD)(PMe_3)_3]Cl$ leading to the formation of *mer*-$IrH(Ph)(Cl)(PMe_3)_3$ (**1**). **1** will undergo further reaction with 2-butyne upon chloride removal to yield $[Ir(Ph)(methallyl)(PMe_3)_3][PF_6]$ (**2**). **2** has been characterized by X-ray crystallography. Insertion of 2-butyne into the Ir–H bond of **1** followed by β-hydride elimination to yield an (allene)hydridoiridium complex appear to be key features in the formation of **2**. This reaction sequence brings us a step closer to fully functionalizing hydrocarbons following C–H addition.

The marked activity in the area of carbon–hydrogen bond cleavage at transition-metal centers (C–H activation) has led to the discovery of literally dozens of systems that are capable of adding alkane and arene C–H bonds.[1] However, with a few notable exceptions,[2] the chemistry stops at the initial C–H addition step: attempts to functionalize the metal hydrocarbyl fragment for the most part have been unsuccessful. There are many reasons for this lack of success, but most prominent among them is the nature of the hydridometal hydrocarbon grouping. In many cases, addition of reagents intended to induce further reaction of the complex results in reductive elimination to nonproductively re-form the original hydrocarbon.[3] This communication reports on a system in which further reactions of the C–Ir–H species formed by addition of a C–H bond to an iridium complex are made facile by chemical removal of a chloride ligand.

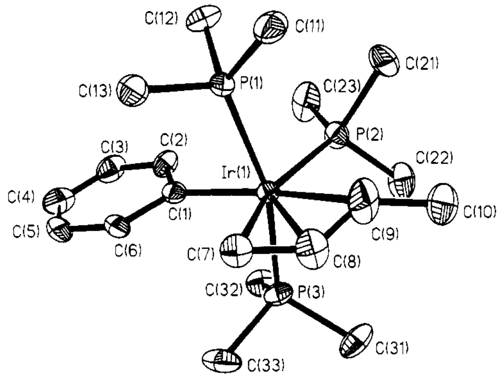
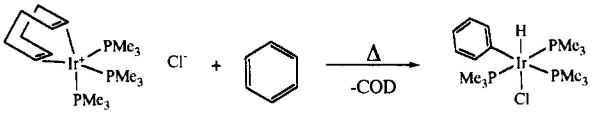


Figure 1. ORTEP plot of the phenyl(methallyl)tris(trimethylphosphine)iridium cation of **2**. Important bond distances (Å): Ir(1)–P(1) = 2.351 (2), Ir(1)–P(2) = 2.328 (2), Ir(1)–P(3) = 2.350 (2), Ir(1)–C(1) = 2.118 (6), Ir(1)–C(7) = 2.208 (7), Ir(1)–C(8) = 2.190 (9), Ir(1)–C(9) = 2.36 (1), C(7)–C(8) = 1.35 (1), C(8)–C(9) = 1.27 (1), C(9)–C(10) = 1.44 (1). Important bond angles (deg): P(1)–Ir(1)–P(2) = 93.0 (1), P(1)–Ir(1)–P(3) = 163.3 (1), P(2)–Ir(1)–P(3) = 94.0 (1), P(1)–Ir(1)–C(1) = 82.3 (2), P(2)–Ir(1)–C(1) = 104.2 (2), P(3)–Ir(1)–C(1) = 81.2 (2), P(1)–Ir(1)–C(7) = 88.0 (2), P(2)–Ir(1)–C(7) = 156.6 (2), P(3)–Ir(1)–C(7) = 91.6 (2), P(1)–Ir(1)–C(8) = 101.2 (3), P(2)–Ir(1)–C(8) = 121.6 (3), P(3)–Ir(1)–C(8) = 88.0 (3), P(1)–Ir(1)–C(9) = 62.6 (3), P(2)–Ir(1)–C(9) = 91.7 (3), P(3)–Ir(1)–C(9) = 102.3 (3), Ir(1)–C(7)–C(8) = 71.3 (5), C(7)–C(8)–C(9) = 138.6 (10) C(8)–C(9)–C(10) = 135.4 (10).

Heating a slurry of tris(trimethylphosphine)(cyclooctadiene)iridium chloride,[4] $[Ir(COD)(PMe_3)_3]Cl$, in benzene leads to loss of cyclooctadiene and the addition of benzene to yield *mer*-hydridophenylchlorotris(trimethylphosphine)iridium, $Ir(H)(Ph)(Cl)(PMe_3)_3$ (**1**) (eq 1).



(1)

Compound **1** was identified on the basis of its elemental analysis, ^1H and ^{13}C NMR spectra, and single-crystal X-ray structure.[5] One interesting feature of **1** is an extremely large barrier to rotation about the iridium–phenyl bond as evidenced by the inequivalence of all five phenyl hydrogens in the ^1H NMR spectrum and all six phenyl carbons in the ^{13}C NMR spectrum. This feature will be

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(1) Some important references are: (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984, and references therein. (b) Bergman, R. G. *Science* **1984**, *223*, 902. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (d) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. M.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814. (f) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (g) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449. (h) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(2) Some references on functionalization in systems involving oxidative addition of a C–H bond are: (a) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1987**, *6*, 696. (b) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, 1279. (c) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 5640. (d) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (f) Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047. (g) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (h) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

(3) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(4) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(5) Approximately 1.0 g (1.77 mmol) of $[Ir(COD)(PMe_3)_3]Cl$ was slurried in 50 mL of benzene and sealed in a pressure tube. The slurry was heated to 150 °C overnight, at which time all material had dissolved to yield a pale yellow solution. Removal of the benzene under vacuum yielded a pale yellow solid. Washing of the solid with small amounts of pentane removed what appears to be a low yield of *fac*-$IrH(Ph)(Cl)(PMe_3)_3$ identified only by ^1H NMR spectroscopy. The bulk of the material was 0.55 g (1.03 mmol, 58% yield) of *mer*-$IrH(Ph)(Cl)(PMe_3)_3$ (1), a pentane-insoluble off-white solid. Anal. Calcd (found) for $C_{15}H_{33}ClIrP_3$: C, 33.74 (33.35); H, 6.23 (6.25); Cl, 6.64 (6.91); Ir, 35.99 (36.05); P, 17.40 (16.98). ^1H NMR (C_6D_6): δ −23.46 (q, J_{P-H} = 4.6 Hz, 1 H, Ir–H), 1.23 (t, J_{P-H} = 2.9 Hz, 18 H, trans PMe_3), 1.58 (d, J_{P-H} = 7.7 Hz, 9 H, cis PMe_3), 6.7–6.9 (complex set of three pseudotriplets, 3 H, phenyl), 7.39 (pseudotriplet, 1 H, phenyl), 8.15 (pseudotriplet, 1 H, phenyl). The single-crystal X-ray structure of 1 confirmed the *mer* stereochemistry. Details of the structure determination will be included in the full paper.

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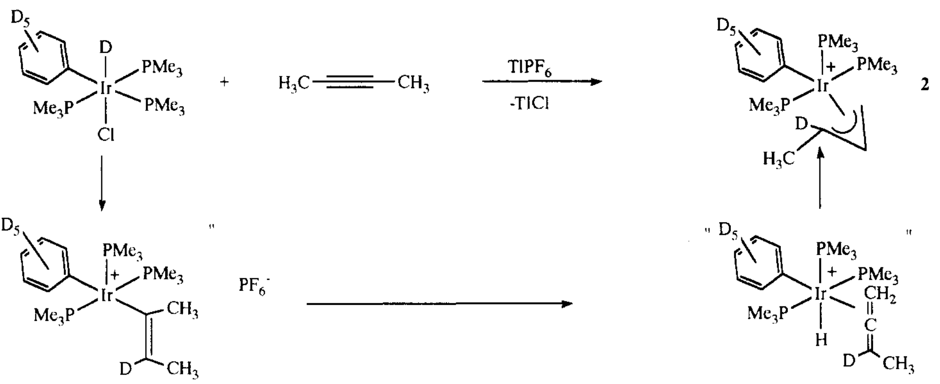
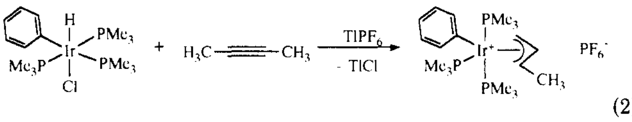
Scheme I



discussed in greater detail in a full report of this work.[6]

While the above reaction represents a novel addition to the number of recent systems capable of *thermal* C–H bond activation,[7] the uniqueness of the system arises from the ability to carry out further reactions on the system. The chloride ligand in **1** provides us with a group that can be chemically removed under mild conditions in the presence of potential functionalizing reagents. The most intriguing results to date come from the removal of the chloride in the presence of acetylenes. Using thallium hexafluorophosphate, $Tl^+PF_6^-$, to remove the chloride ligand from **1** (as insoluble TlCl) in a reaction mixture containing 2-butyne results in the immediate formation of the methallyl complex phenyl(methallyl)tris(trimethylphosphine)iridium hexafluorophosphate, $[Ir(Ph)(methallyl)(PMe_3)_3][PF_6]$ (**2**) (eq 2).



(2)

The analytical data indicated that **2** was most likely a methallyl compound,[8] and a single-crystal X-ray diffraction study of **2** confirmed this assignment. The ORTEP plot of the resulting structure is shown in Figure 1.[9] The overall geometry of **2** can be described as a distorted octahedron with the three PMe_3 ligands situated in a meridional arrangement and the phenyl group cis to all three phosphines. The remaining two octahedral sites are taken up by the methallyl ligand with the methyl end cis to the three phosphine ligands. The allyl ligand is coordinated unsymmetrically to the iridium with the C–C bond trans to the phenyl group shorter (1.272 (15) Å) than the C–C bond trans to a PMe_3 (1.354 (13) Å), and the Ir–C(9) distance (C trans to phenyl) of 2.361 (11) Å is longer than the Ir–C(7) (C trans to PMe_3) distance of 2.208 (7) Å. Both of these point to a stronger trans influence for phenyl than for PMe_3, resulting in more of a σ–π coordination for the allyl ligand.[10] The PF_6^- counterion displayed rather large thermal ellipsoids, not uncommon with PF_6^- or BF_4^-, and was otherwise unexceptional.

Deuterium labeling experiments pointed to the sequence of steps shown in Scheme I as the likely mechanism for the formation of **2**. Using C_6D_6 in place of C_6H_6 affords the deuterated analogue of **1**, $Ir(D)(C_6D_5)(Cl)(PMe_3)_3$. Following chloride removal, 2-butyne "inserts" in the Ir–D bond of **1** to form an iridium 1,2-dimethylvinyl complex. This material is not observed, but it is presumed that a β-hydride elimination from the β-methyl group occurs, forming a hydridoiridium allene complex. Readdition of hydride to the center carbon of the allene then generates the observed methallyl complex. The position of the deuterium on the same allyl carbon as the methyl group in the final product is consistent with the pictured scheme. Rearrangement of a σ methylvinyl to an allyl has been observed in other systems,[11] and our studies on the mechanism are consistent with those reported by Werner.[11a] This appears to be a general reaction with alkynes possessing hydrogens on carbon α to the triple bond. Thus, the reaction of **1** with 3-hexyne following chloride removal by $TlPF_6$ leads to the formation of a 1-methyl-3-ethylallyl complex, **3**.[12]

The utility of this reaction sequence is that the metal hydride formed in the C–H addition step has been "functionalized" and the problem of nonproductive back-

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(6) Hindered rotation in a series of octahedral phenylruthenium complexes has been reported: Probitts, E. J.; Saunders, D. R.; Stone, M. H.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1167.

(7) Some other examples of thermal addition of benzene C–H bonds are: (a) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090. (b) Hacket, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436.

(8) **1** (0.5 g, 1 mmol) was dissolved in 20 mL of CH_2Cl_2. An excess of 2-butyne was added, followed by 0.35 g (1 mmol) of $TlPF_6$. The reaction mixture was stirred for 1 h, at the end of which time the insoluble TlCl was removed by filtration through a fine frit. Diethyl ether was slowly added to the filtrate to precipitate the product, which was collected to yield 0.55 g (0.78 mmol, 78% yield) of **2**. Anal. Calcd (found) for $C_{19}H_{39}F_6IrP_4$: C, 32.71 (32.66); H, 5.63 (5.55); P, 17.76 (18.01). ^1H NMR (CD_2Cl_2, atom numbers refer to ORTEP plot of **2**): δ 1.24 (m, 18 H, trans PMe_3), 1.58 (d of d, $J_1 = 4.4$ Hz, $J_2 = 1.8$ Hz, 3 H, allyl methyl), 1.80 (d, $J_{P-C} = 8.5$ Hz, 9 H, cis PMe_3), 2.64 (m, 1 H, one H on C(7) of allyl; other H on C(7) is obscured by phosphine resonance), 3.05 (m, 1 H, H on C(8) of allyl), 4.67 (m, 1 H, H on C(9) of allyl), 6.90–7.70 (m, 5 H, phenyl).

(9) Crystal structure data for **2**, $C_{19}H_{39}F_6P_4Ir$: Crystals were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **2**. The crystals belong to the monoclinic space group $P2_1/c$, with $a = 10.098$ (2) Å, $b = 17.156$ (3) Å, $c = 15.506$ (3) Å, $\beta = 92.16$ (2)°, $V = 2684.3$ (9) Å^3, and $d_{calcd} = 1.726$ g cm^{-3} for $Z = 4$. Data were collected at 298 K on a Nicolet R3m/V diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan technique. A total of 4755 reflections were collected with 4092 observed ($F > 3.0\sigma(F)$). A semiempirical absorption correction was applied to the data ($\mu = 5.236$ mm^{-1}) on the basis of a series of ψ scans. The structure was solved by using Patterson methods and refined by using full-matrix least-squares procedures employing the SHELXTL-Plus software as supplied by Nicolet Corp. The solution was refined with the final residuals $R = 0.0365$ and $R_w = 0.0481$.

(10) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227.

(11) (a) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. (b) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (c) This rearrangement has also been observed in trimetallic clusters: Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385.

(12) **3** was synthesized in 54% yield in a manner identical with that employed to synthesize **2**. Anal. Calcd (found) for $C_{21}H_{43}F_6IrP_4$: C, 34.76 (34.91); H, 5.97 (6.41); P, 17.07 (16.73). ^1H NMR (CD_2Cl_2, numbers refer to *analogous* carbons in ORTEP plot of **2**): δ 1.00 (t, $J = 7.2$ Hz, 3 H, CH_3CH_2-allyl), 1.24 (br d, $J_{P-C} = 6.5$ Hz, 18 H, trans PMe_3), 1.80 (d, $J_{P-C} = 8.5$ Hz, 9 H, cis PMe_3), 2.66 (m, 1 H, one H on C(7) of allyl), 2.99 (m, 1 H, H on C(8) of allyl), 4.67 (m, 1 H, H on C(9) of allyl), 6.80–7.70 (m, 5 H, phenyl), CH_3CH_2-allyl and CH_3-allyl protons obscured by PMe_3 resonances.

elimination has been blocked. To close the loop, it remains for us to find suitable conditions to induce reductive elimination of the hydrocarbon fragments.[13] Further investigations of this system are planned in order to develop metal complexes suitable for such sequential C–H addition and functionalization reactions of both alkanes and arenes.

Acknowledgment. I gratefully acknowledge financial support from the Thomas F. Jeffress and Kate Miller Jeffress Memorial Trust.

Supplementary Material Available: A listing of ^{13}C and ^{31}P NMR spectral data for **1–3**, an ORTEP plot of the PF_6^- anion in **2**, and listings of final atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for **2** (6 pages); a listing of observed and calculated structure factors for **2** (17 pages). Ordering information is given on any current masthead page.

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(13) Our preliminary experience suggests that both thermally induced coupling and chemically induced coupling are possible. For example, heating a solution of **2** at 100 °C with PMe_3 overnight leads to a complex mixture of products, but the proton NMR spectrum of the olefinic region is consistent with having products derived from phenyl coupling with the methallyl group. The same is true for the treatment of **2** with anhydrous $ZnBr_2$ in CH_2Cl_2.

Book Reviews

Sonochemistry: Theory, Applications, and Uses of Ultrasound in Chemistry. By T. J. Mason and J. P. Lorimer. Ellis Harwood Ltd., Chichester, England, and J. Wiley & Sons, New York. 1988. xii + 252 pp. 17 × 25 cm. ISBN 0-7458-0240-0. $87.95.

The chemical effects of ultrasound arise primarily from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in irradiated liquids. During the collapse, intense local heating (≈5000 K) and high pressures (≈1000 atm) are produced for a few microseconds. This hot-spot is responsible for most homogeneous sonochemistry. The shock waves and impacting jets of liquid produced by cavitational collapse are responsible for most of the effects of ultrasound on the reactivity of solids.

The chemical effects of ultrasound were first recognized by A. L. Loomis in 1927. Only during the past half-dozen years, however, has sonochemistry emerged as a viable research topic and become a useful tool for synthesis and mechanistic studies. The growth of the field has been tremendous. A wide range of organometallic applications have been demonstrated, including ligand substitution, initiation of both homogeneous and heterogeneous catalysis, and its general use in almost any solid–liquid two-phase reaction. Numerous reviews of the field have been published, for instance, in *Adv. Organomet. Chem.*, *Chem. Soc. Rev.*, *J. Chem. Educ.*, *Mod. Synth. Methods*, and even *Sci. Am.* There have been sonochemical symposia at major international conferences, including the Royal Society of Chemistry meeting in 1986 and the Pacifichem '89 meeting. Thus, it is appropriate that there now should begin to appear specialized monographs on the chemical effects of ultrasound.

This book is a survey of the chemical effects of ultrasound. Since this is one of the first two modern monographs on the topic in English, the authors are breaking new ground and deserve praise for their attempt. This work is an introductory text rather than a comprehensive research tool. There are eight chapters: Ultrasonics, General Principles, Synthesis, Polymers, Kinetics and Mechanisms, High Frequency Ultrasound, Ultrasonic Equipment and Chemical Reactor Design, and Miscellaneous. References appear at the end of each chapter, are current through 1987, and total 291; this is a reasonable sampling of the literature but represents less than a third of the relevant citations.

Unfortunately, there are a number of weaknesses in the text. Some of these are problems with the editing. The figures and chemical formulae can be a bit spotty; most are done well, but some are substandard; often the figures are disproportionately large. There are more than a few typographic errors, particularly among the references. In addition, the price of the volume is quite high, especially considering the introductory nature of the text.

Other problems are simply organizational. For example, there is significant crossover in content from chapter to chapter, and the undetailed table of contents and the limited subject index make it difficult to find things. The lack of an author index contributes further to this problem.

Some of the problems, however, lie in the text's content. The relative weights of various topics are not always well balanced between the authors' and others' work. More seriously, explanations and conclusions are sometimes presented which are at best controversial, at least to this reviewer. This may be a necessary consequence for an early text in an emerging field where a dominant paradigm is not yet fully established. Sonochemistry remains in its infancy, and there are still fundamental matters where consensus is yet to be achieved.

Newcomers to the field may wish to start with this book, bearing in mind the caveats already mentioned, or they may do better with one of the other recent reviews or monographs. Workers in this area will probably want to have their own copy.

Kenneth S. Suslick, *University of Illinois at Urbana-Champaign*

Stereochemical Applications of Gas-Phase Electron Diffraction. Edited by I. Hargittai and M. Hargittai. VCH Publishers, Inc., New York. 1988. Part A: The Electron Diffraction Technique (538 pp). Part B: Structural Information for Selected Classes of Compounds (474 pp). $100/volume.

The editors' objective was to assemble a definitive summary of the current status of gas-phase electron diffraction (GED). In this they have succeeded. The first volume incorporates reviews of all aspects of the theory of multi-kiloelectron volt scattering by molecules and analyses of the complementarity with respect to structure determination, of GED, of spectroscopy (high-resolution IR; microwave; NMR), and of molecular orbital computations. In the second volume structural data for nine classes of molecules are summarized; these are arranged according to distinctive elements (or structural features). The formula index of Part B contains approximately 1500 entries (about half of all structures ever determined by GED); some of these also appear in the considerably shorter formula index of Part A. Overall the material is well organized; the tables and figures are informative. Care was taken by the individual authors to correlate GED results within members of each class and with values derived from other sources along with listings of the precision claimed by the original investigators. Kuchitsu, Nakata, and Yamamoto summarized relations between measured (averaged) atom-pair separations deduced by combining GED and microwave spectroscopy to derive "best" structural parameters; 120 molecules have been subjected to such a "joint" analysis. As a compendium of molecular structural data for gas-phase species these two volumes will prove most useful, as will the extensive list of references.

On leafing through volume A one quickly notices a significant number of repetitions of basic equations and familiar discussions of the effects of molecular dynamics on the recorded diffraction patterns. The unscrambling of intramolecular motions, whether harmonic, anharmonic, or perturbed by "large amplitude motions",