argument that in TBP complexes the π-back-bonding with e′ d orbitals is stronger than that with e″ d orbitals, due to the favorable mixing of equatorial 4p orbitals of the metal.[12] We believe that this discrepancy is a consequence of incomplete geometry optimizations: since the geometry of the free olefin corresponds more closely to that of the weakly complexated one, it precludes an adequate description of the forward- and back-bonding of the π orbitals. This omission has a potential for reversing the already close energy levels of the two conformations.

By the same token, comparison with Zeise's anion, $[Pt(C_2H_4)Cl_3]^-$, made by Grima et al.[16,26] to the effect that the geometry of the olefin should not change much because of complexation is not entirely justified. In this anion, the platinum atom has an approximate D_{4h} coordination, in which the p orbitals belong to symmetry types a_{2u} and e_u, different from the symmetry types of d orbitals (a_{1g}, b_{1g}, b_{2g}, and e_g). This hinders the 4p-orbital enhancement of the π-back-bonding,[12] which is symmetry-allowed in the D_{3h} coordination and which our calculations confirm.

Acknowledgment. This paper is based upon work supported by the National Science Foundation under Grants No. CHE-83-09446, CHE-84-05851, and CHE-85-03415. We also wish to acknowledge the NSF support for the calculations done on the Cyber 205 supercomputer at Purdue University in West Lafayette, IN.

Supplementary Material Available: Bond lengths and bond angles (Table I) and frontier orbitals (Table III) of the closed-shell configurations of $CHO{-}Co(CO)_3$, bond lengths and bond angles (Table V) and frontier orbitals (Table VII) of the closed-shell configurations of $HCo(CO)_3{-}C_2H_4$, bond lengths, bond angles, and SCF energies of the conformations of $CH_3CH_2Co(CO)_3$ (Table VIII), CI energies of the closed-shell configurations of $HCo(CO)_3{-}C_2H_4$ and $CH_3CH_2Co(CO)_3$ (Table IX), summary of the results on ethylene ^1A_g (3-21G basis) (Table 10), and density difference of the CC (Figure 30) and EtC (Figure 31) conformations of $HCo(CO)_3{-}C_2H_4$ in the symmetry plane (25 pages). Ordering information is given on any current masthead page.

---

(26) Rösch, N.; Messmer, R. P.; Johnson, K. D. *J. Am. Chem. Soc.* **1974**, *96*, 3855.

(27) Daniel, C.; Hyla-Kryspin, J.; Demuynek, J.; Veillard, A. *Nouv. J. Chim.* **1985**, *9*, 581. This important reference has studied H and CO dissociation from $HCo(CO)_4$ with configuration interaction methods.

Communications to the Editor

Molybdenum and Tungsten Derivatives of 2,6-Diphenylphenoxide: Chelation via Metal-Carbon σ-Bonds or Metal-π-Arene Interactions

Judith L. Kerschner, Phillip E. Fanwick, and
Ian P. Rothwell*[1]

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received April 23, 1987

The early transition-metal chemistry associated with 2,6-dialkylphenoxide and 2,6-dialkylthiophenoxide ligation has recently received considerable research interest.[2-6] Following our studies of the sometimes mild intramolecular activation of the aliphatic carbon-hydrogen bonds in 2,6-di-*tert*-butylphenoxide ligands,[7] we have turned our attention to the organometallic chemistry associated with 2,6-diphenylphenoxide groups.[8] This ligand also

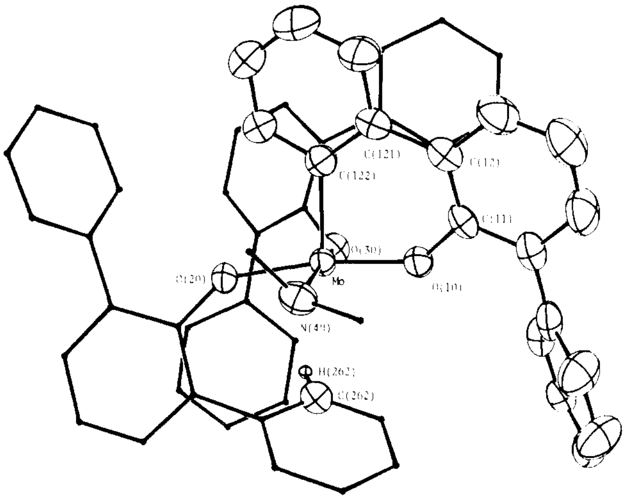


Figure 1. ORTEP view of **1** emphasizing the central coordination sphere and metallacycle ring. Selected bond distances (Å) and angles (°) are are follows: Mo-O(10), 1.919 (2); Mo-O(20), 1.976 (2); Mo-O(30), 1.962 (3); Mo-N(40), 2.288 (4); Mo-C(122), 2.075 (4); Mo-C(262), 2.814 (5); Mo-H(262), 2.67 (5); O(10)-Mo-O(20), 165.8 (1); -O(30), 97.9 (1); -N(40), 87.3 (1); -C(122), 86.4 (1); C(122)-Mo-C(262), 174.5 (1), -H(262), 164 (1).

---

(1) Camille and Henry Dreyfus Teacher-Scholar, 1985-1990. Fellow of the Alfred P. Sloan Foundation, 1986-1990.

(2) (a) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. (b) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155. (c) Chamberlain, L. R.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1987**, 163. (d) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1986**, *4*, 902. (e) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

(3) (a) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (b) Latham, I. A.; Sita, L. R.; Schrock, R. R. *Organometallics* **1986**, *5*, 1508. (c) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2161. (d) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

(4) (a) Duff, A. W.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 489 and references therein. (b) Dilworth, J. R.; Hanich, J.; Krestel, M.; Beuk, J.; Strahle, J. *J. Organomet. Chem.* **1986**, *315*, C9.

(5) (a) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121. (b) Blower, P. J.; Dilworth, J. R.; Zubieta, J. *Inorg. Chem.* **1985**, *24*, 2866. (c) Bishop, P. T.; Blower, P. J.; Dilworth, J. R.; Zubieta, J. A. *Polyhedron* **1986**, *5*, 363. (d) Bishop, P. T.; Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 257. (e) Bishop, P. T.; Dilworth, J. R.; Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1123. (f) Blower, P. J.; Bishop, P. T.; Dilworth, J. R.; Hsieh, T. C.; Hutchinson, J.; Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1985**, *101*, 63. (g) Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2639. (h) Burt, R. J.; Dilworth, J. R.; Leigh, G. J. Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1982**, 2295.

(6) (a) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795. (b) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207. (c) Fikor, R.; Koch, S. A.; Miller, M. M. *Inorg. Chem.* **1985**, *24*, 3311. (d) Soong, S. L.; Chebolv, V.; Koch, S. A.; O'Sullivan, T.; Miller, M. M. *Inorg. Chem.* **1986**, *25*, 4067.

(7) (a) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (b) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. (c) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (d) Chamberlain, L.; Rothwell, I. P. *J. Am. Chem. Soc.* **1983**, *105*, 1665.

0002-7863/87/1509-5840$01.50/0

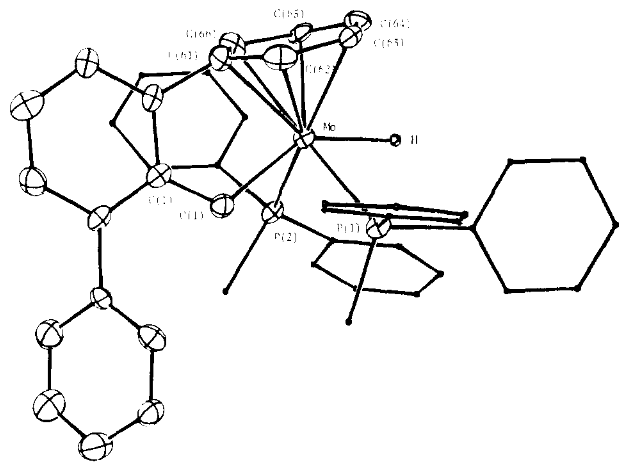
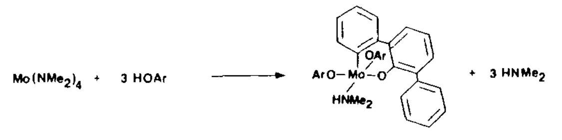


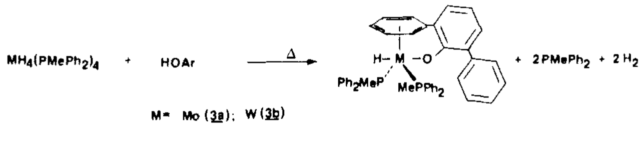
Figure 2. ORTEP view of **3a** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (°) are as follows: Mo–P(1), 2.45 (2); -P(2), 2.453 (2); -O(1), 2.164 (5); -C(61), 2.262 (7); -C(62), 2.329 (7); -C(63), 2.255 (6); -C(64), 2.313 (7); -C(65), 2.301 (8); -C(66), 2.238 (7); Mo–H, 1.164 (8); Mo–O(1)–C(1), 118.0 (4).

offers the potential for metallacycle formation albeit via activation of an aromatic CH bond. We communicate here our initial findings concerning the coordination of this ligand to the heavier group 6 metals that indicate not only that formation of new metal–carbon σ-bonds is possible but that ground-state metal–arene interactions can also be present.

The addition of 2,6-diphenylphenol (HOAr) to the deep purple $Mo(NMe_2)_4$[9] in benzene results in the formation of a deep red, crystalline precipitate **1** after several hours. Microanalytical data on the sparingly soluble **1** indicated a stoichiometry "$Mo(OAr)_3(NMe_2)$".[10] However, infrared data on **1** is inconsistent with this simple formulation showing a sharp band at 3250 cm^{-1} assignable to $\bar{\nu}$(NH) of a dimethylamine ligand.[10] A solid state crystal structure of **1**[11] confirmed the presence of an $HNMe_2$ group formed by the cyclometalation of one of the 2,6-diphenylphenoxide ligands (Figure 1). The geometry about the Mo atom can be seen to be square pyramidal with the metalated carbon atom occupying the axial site. The almost planar six-membered metallacycle comfortably maintains an 86° bite at the metal center due to the large Mo–O–C angle of 145°. Substitution of the $HNMe_2$ ligand by pyridine (py) is easily achieved to yield the monoadduct **2**.[12] No evidence to support the formation of a six-coordinate, bis adduct has been obtained. A study of the coordination environment about the molybdenum atom in **1** shows a close approach of an aromatic CH bond of a nonmetalated OAr group in the vacant, axial position almost exactly trans to the Mo–C bond (Figure 1). The distances to this bond are refined as Mo–H = 2.67 (5) Å and Mo–C = 2.814 (5) Å, with the CH approaching the metal in a side-on fashion with Mo-H-C = 91 (3)°. However, the distances to this group are certainly on the outer fringes of those reported for well documented agostic interactions.[13-15]



Reaction of the tetrahydrides $MH_4(PMePh_2)_4$ (M = Mo, W)[16] with ArOH again does not lead to simple substitution products. Extended thermolysis (phenol melt, 150 °C) results in formation of a deep red mixture from which red crystals of a product of stoichiometry "$M(OAr)(PMePh_2)(H)$" (M = Mo, **3a**; W, **3b**) are obtained.[17] A single-crystal X-ray analysis (Figure 2) shows the phenoxide ligands in **3** to again be chelated to the metal, only this time via an η^6-interaction through one of the ortho phenyl substituents.[19,20] The ^1H NMR spectra of these 18-electron monohydrides show a sharp set of three upfield resonances (ratio 2:2:1) for the π-ring indicating the ortho and meta protons are equivalent, as well as a triplet for the M–H hydride.[17] There is no indication of rapid exchange of coordinated and noncoordinated orthophenyl rings.[20] A structural study on **3a** (Figure 2)[18] confirmed the presence of the phenoxide chelate and also managed to identify the hydride position. This position is entirely consistent with the spectroscopic data indicating a virtual plane of symmetry in the molecule equilibrating the phosphine ligands and both sides of the π-bound arene ring. The Mo–O distance of 2.163 (11) Å in **3a** is significantly longer than the distances of 1.92–1.96 Å found in **1** and can be rationalized by recognizing the necessary absence of any oxygen-p to metal-d π-bonding in the 18-electron derivatives **3**. The Mo–C distances found to the π-bound arene ring in **3a**, 2.25–2.34 Å, are comparable to those reported for other molybdenum η^6-arene compounds.[5c,20] However, these distances are much shorter than those found for the close aromatic CH bond



---

(8) (a) Ogilvy, A. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 72. (b) Coffindaffer, T. W.; Westler, W. M.; Rothwell, I. P. *Inorg. Chem.* **1985**, *24*, 4565.

(9) (a) Chisholm, M. H.; Reichert, W. W.; Thorton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744. (b) Addition of 2,6-dialkylphenols to both $Mo(NMe_2)_4$ and $MoH_4(PMe_2Ph)_4$ has been shown to yield simple substitution products, see: Beshouri, S. M.; Coffindaffer, T. W.; Pirzad, S.; Rothwell, I. P. *Inorg. Chim. Acta.* **1985**, *103*, 111.

(10) Anal. Calcd for $MoC_{56}H_{48}NO_3$: C, 76.77; H, 5.18; N, 1.59. Found: C, 77.40; H, 5.24; N, 1.90. Infrared (Nujol mull): $\bar{\nu}$(N–H) = 3250 cm^{-1}.

(11) Crystal data for $MoC_{59}H_{48}NO_3$ (**1**) at 22 °C: space group $P\bar{1}$, a = 13.431 (2) Å, b = 18.213 (5) Å, c = 10.262 (1) Å, α = 101.68 (2), β = 106.53 (1), γ = 77.93 (2)°, Z = 2, d_{calcd} = 1.306 g cm^{-3}. A total of 6113 unique data was collected with Mo Kα radiation, $4° \leq 2\theta \leq 45°$ of which 4625 with $I > 3\sigma(I)$ were used in the final refinement to yield residuals of R = 0.038, R_W = 0.054. The hydrogen atoms H(262) and H(N) were refined.

(12) Anal. Calcd for $MoC_{59}H_{43}NO_3$ (**2**): C, 77.88; H, 4.76; N, 1.58. Found: C, 77.74; H, 4.74; N, 1.38.

(13) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein. (b) Dawoodi, Z.; Green, M. L. H.; Metewa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629. (c) Crabtree, R. H.; Holt, E. M.; Larin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

(14) (a) Erker, G.; Fromberg, W.; Angermund, K.; Schlund, R.; Kruger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 372. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725. (c) Colvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (d) Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stuckey, G. D.; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7407. (e) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4542. (f) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (g) Trofimenko, S. *J. Am. Chem. Soc.* **1968**, *90*, 4754. Trofimenko, *Inorg. Chem.* **1970**, *9*, 2483. (h) Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074.

(15) The close approach of CH bonds to various metal centers in derivatives of 2,6-di-*tert*-butylphenoxide complexes have been noticed and discussed, see: Fanwick, P. E.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73.

(16) Crabtree, R. H.; Hltaky, G. G. *Inorg. Chem.* **1982**, *21*, 1273.

(17) Selected spectroscopic data: ^1H NMR (C_6D_6, 30°C) (**3a**) δ −2.92 (t, Mo-*H*), 1.55 (d, P*Me*), 2.87 (t), 3.68 (m), 4.38 (d, the *p*, *m*; and *o*-H of η^6-C_6H_5 ring); (**3b**) δ −1.50 (t, W-*H*), 1.69 (d, P*Me*), 2.69 (t), 3.56 (m), 4.04 (d, the *p*–, *m*–, and *o*-H's of η^6-C_6H_5 ring); ^{13}C NMR (C_6D_6, 30 °C) (**3a**) δ 15.2 (d, P*Me*), 77.9, 79.9, 85.6, 112.7 (the *p*, *m*, *o*, and ipso carbon atoms of the η^6-C_6H_5 ring); (**3b**) δ 12.6 (d, P*Me*), 70.8, 71.9, 78.1, 113.4 (the *p*, *m*, *o*, and ipso carbon atoms of the η^6-C_6H_5 ring); IR (Nujol mull) (**3a**) $\bar{\nu}$(Mo–H) = 1804 cm^{-1}; (**3b**) $\bar{\nu}$(W–H) = 1870 cm^{-1}.

(18) Crystal data for $MoC_{44}H_{40}P_2O$ (**3a**) at −145 °C: space group $P2_1/c$, a = 17.310 (7) Å, b = 10.149 (3) Å, c = 21.090 (5) Å, β = 108.89 (2)°, Z = 4, d_{calcd} = 1.407 g cm^{-3}. A total of 6567 unique data was collected by using Mo Kα radiation, $4° \leq 2\theta \leq 50°$, of which 3709 with $I > 3\sigma(I)$ were used in the final refinement. The hydrogen atom bound to the metal was observed and refined. Final residuals are R = 0.054, R_w = 0.071.

(19) A similar coordination mode for 2,6-diphenylthiophenoxide has been reported by Dilworth et al., see ref 5c, while the metalation of a bridging 2,6-diphenylthiophenoxide at rodium has also been reported, see ref 5a), p 142.

(20) For a general review of group 6 metal–η^6-arene complexes, see: *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press, New York, 1981.

in **1** (vide supra) again implying little if any agostic interaction in the amine compound.

Further studies of the possible mechanism for CH bond activation at these metal centers and the possible interconversion of the chelate types are presently underway.

Acknowledgment. We thank the National Science Foundation (Grant CHE-86120643) to I.P.R. for support of this research. We also thank the National Science Foundation Chemical Instrumentation Program (Grant CHE-8204994) for support of the X-ray diffraction facility at Purdue; I.P.R. also gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher–Scholar Grant and the Alfred P. Sloan Foundation for a fellowship. J.L.K. gratefully acknowledges award of a David Ross Fellowship by the Purdue Research Foundation.

Supplementary Material Available: Tables of positional parameters, general temperature factors, bond distances, and bond angles for **1** and **3a** (28 pages); listing of structure factor amplitudes for **1** and **3a** (36 pages). Ordering information is given on any current masthead page.

Two-Dimensional Coherence Transfer NMR Spectroscopy by Isotropic Mixing: Application to Protein NMR Assignments

Paul L. Weber,[1a,e] Larry C. Sieker,[1b] T. S. Anantha Samy,[1d] Brian R. Reid,[1a,c] and Gary P. Drobny*[1c]

Department of Biochemistry
The University of Washington
Seattle, Washington 98195

Received August 29, 1986

Homonuclear spin-locking with matched Hartmann–Hahn radio frequency fields to obtain long-range coherence transfer within spin systems has received much attention recently.[2-5] The 2D NMR experiments, often referred to as rotating frame, isotropic mixing, "TOCSY",[2] or "HOHAHA"[4] experiments, have considerable potential for identifying long amino acid side-chain systems in proteins (e.g., lysine, leucine, arginine, et al.). This is in contrast to the RELAY experiment,[6,7] where the mixing time must be tuned for optimal relayed intensity for different spin systems,[8,9] and generally only single-step relays can be obtained with good signal intensity for larger proteins due to relaxation limitations. As discussed below, however, there are still compelling reasons for performing RELAY experiments in conjunction with isotropic mixing experiments.

First we demonstrate the results of applying WALTZ-16[10] and MLEV-16[11] pulse sequences to obtain long-range coherence transfers (Figure 1). Each spectrum was obtained under identical conditions on our home-built 500-MHz spectrometer[12] using a 20-W pulse for both the preparation and 40-ms mixing pulses, corresponding to an applied radio frequency field of 16–20 kHz. Bax and Davis[3] have modified the MLEV-16 pulse sequence by incorporating a 180° refocusing pulse and straddling "purge" pulses to correct for pulse imperfections and to eliminate antiphase and dispersive magnetization. These errors do not appear to dominate isotropic mixing spectra when the applied radio frequency field is sufficiently strong; thus the purge pulses are not required for obtaining good quality spectra. Note also that the

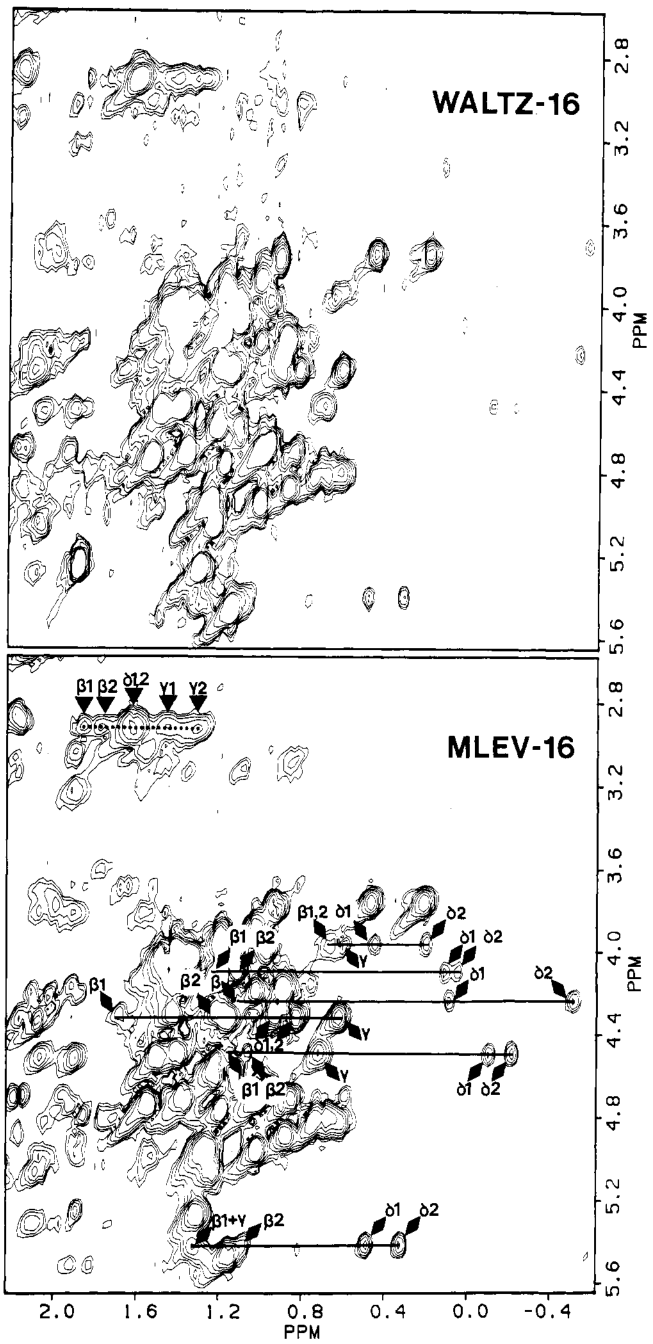


Figure 1. Selected regions of 2D isotropic mixing experiments using WALTZ-16 (above) and MLEV-16 (below) pulse cycling during the spin-locking period and performed off-resonance with 10-kHz spectral widths in both dimensions. 400 t_1 experiments were collected, zero-filled, and transformed, to generate a 1K × 1K matrix. The sample was 8 mM apoNeocarzinostatin (113 amino acids, MW 11 500) in 100% D_2O; spectra were recorded at 45 °C. The six leucine and unique lysine side-chain spin systems are indicated.

---

[1] (a) Department of Biochemistry. (b) Department of Biological Structure. (c) Department of Chemistry. (d) Comprehensive Cancer Center, University of Miami School of Medicine, Miami, FL 33103. (e) Present address: Smith Kline and French Labs L940, 709 Swedeland Road, Swedeland, PA 19479.

[2] Braunschweiler, L.; Ernst, R. R. *J. Magn. Reson.* **1983**, *53*, 521–528.

[3] Bax, A.; Davis, D. G. *J. Magn. Reson.* **1985**, *65*, 355–360.

[4] Davis, D. G.; Bax, A. *J. Am. Chem. Soc.* **1985**, *107*, 2820–2821.

[5] Waugh, J. S. *J. Magn. Reson.* **1986**, *68*, 189–192.

[6] Bolton, P. H. *J. Magn. Reson.* **1982**, *48*, 336–340.

[7] Eich, G.; Bodenhausen, G.; Ernst, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3731.

[8] Bax, A.; Drobny, G. *J. Magn. Reson.* **1985**, *61*, 306–320.

[9] Weber, P. L.; Drobny, G.; Reid, B. R. *Biochemistry* **1985**, *24*, 4549–4552.

[10] Shaka, A. J.; Keeler, T.; Frenkiel, T.; Freeman, R. *J. Magn. Reson.* **1983**, *52*, 335–338.

[11] Levitt, M. H.; Freeman, R.; Frenkiel, T. *J. Magn. Reson.* **1982**, *47*, 328–330.

[12] Gladden, J.; Drobny, G., in preparation.

0002-7863/87/1509-5842$01.50/0