Pyrazolyl-Bridged Iridium Dimers. 16.[1] The Atropisomeric (C_2) System $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$. Synthesis of Homologous Diastereomeric Complexes That Undergo Slow Stereomutation by Ring Inversion of the Bridging Framework: Mechanistic Implications for Bimetallic Substrate Activation

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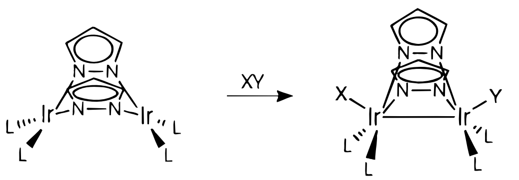
Summary: The diiridium(I) complex $[Ir(P\{OR^*\}Ph_2)(CO)(\mu\text{-pz})]_2$ *(R* = Bor,* ***4a,b****, OBor = (1S)-endo-(−)-bornoxy) exists as two diastereomers (63:37 ratio,* ^1H *and* ^{31}P *NMR) that are found to cocrystallize, providing a source of* ***4a,b*** *in nonequilibrium distribution. NMR measurements show that MeI adduct formation to give the diastereomeric pair of diiridium(II) adducts* ***7a,b*** *is orders of magnitude faster than ring inversion that interconverts* ***4a*** *and* ***4b*** *and that* ***7a,b*** *equilibrate much more slowly than the* ***4a−4b*** *interconversion in a manner that implicates reductive elimination of MeI.*

Oxidative-addition/reductive-elimination processes are crucial in homogeneously catalyzed transformations that begin by attachment of a reactive substrate at an isolated, coordinatively unsaturated transition-metal center.[2] The role of mononuclear rhodium(I) complexes (d^8) in olefin hydrogenation and hydroformylation has become a paradigm in this context[3] because detailed kinetics data are available to decipher the progression of molecular steps that combine to close the catalytic cycle. Similar studies on related systems support a coherent mechanistic view of oxidative addition mediated at a single metal site.[2,4] In contrast, how corresponding two-center chemistry operates is still very poorly defined, despite the implicit significance of binuclear substrate activation as a model for cooperative intermetallic effects.[5] It is particularly difficult to rule out mononuclear character concealed in a dimer fragmentation/activation/recombination sequence. Two-fragment, two-center oxidative addition of substrates XY to the binuclear iridium(I) complex $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$ (**1**, pzH = pyrazole; $d^8{}_2$) is accompanied by metal−metal bond formation (eq 1), affording stable, diamagnetic $d^7{}_2$ adducts; kinetics data have been measured for MeI addition to the analogues $[IrL_2(\mu\text{-pz})]_2$ (**2**, L = CO; **3**, L_2 = COD, (cycloocta-1,5-diene)).[6] Dimer **1** exists as a single isomer with a trans disposition of terminal ligands across a boatlike bridged core:[7] it possesses a stereogenic (C_2) axis and is atropisomeric; thus, it is in principle resolvable (*R*-**1** *vs* *S*-**1**; Scheme 1) and is a prospective target as an enantioselective template. An obvious problem with the latter idea is the possibility of rapid ring inversion of the six-membered cyclic core, which effects racemization (*R*-**1**−*S*-**1**; Scheme 1). By substituting for PPh_3 in **1** using a phosphorus ligand containing an optically pure center, thereby adapting the enantiomeric structure **1** to a diastereomeric pair, we are able to show that substrate addition (using iodomethane as a model) is unequivocally a *bimetallic* event that is over long before inversion of the bridged framework can occur.



(1)

Carbonylation (THF solution) of the precursor **3** to give dimer **2** (which is accompanied[8] by a dramatic color change, from dark brick red to lemon yellow) was followed by addition of bornyl diphenylphosphinite,[9] $P(OBor)Ph_2$ (OBor = (1*S*)-*endo*-(−)-bornoxy), also in THF; gas evolution occurred immediately as the mixture became dark orange. After 30 min, volatile material

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[7] Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R.; Eadie, D. T.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 920; *Inorg. Chem.* **1984**, *23*, 4050.

[8] Harrison, D. G.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1986**, 285.

[9] This compound, which does not appear to have been reported previously, was synthesized by reaction of PPh_2Cl with borneol, in a manner similar to that used to obtain the menthoxyphenylphosphines from (−)-menthol; see: Brunner, H.; Doppelberger, J. *Chem. Ber.* **1978**, *111*, 673. Benes, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2256.

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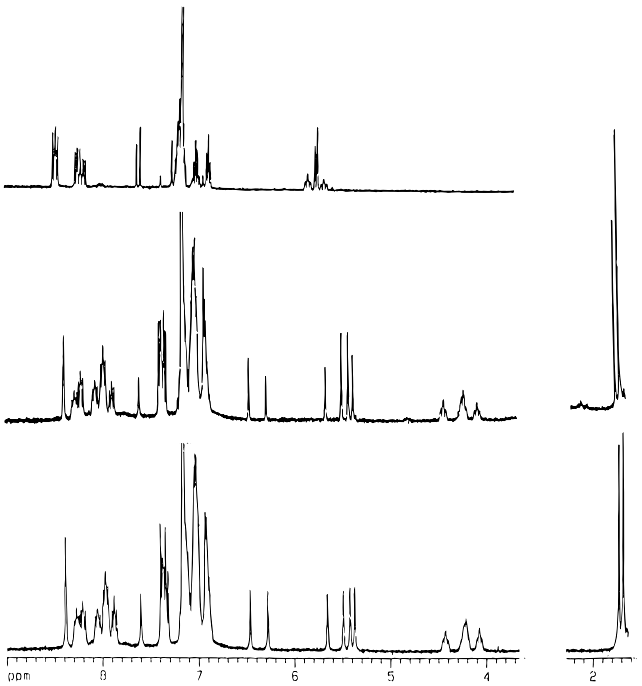
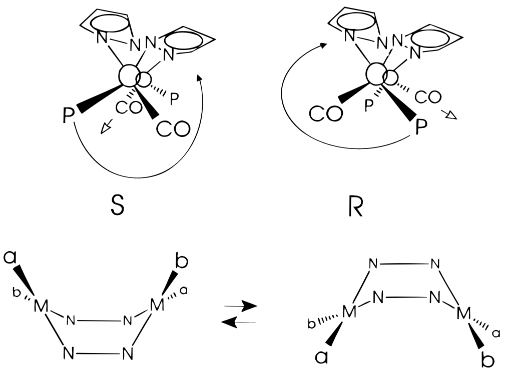
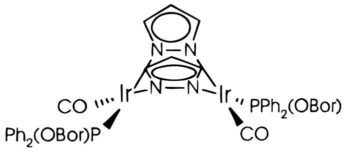


Figure 1. Hydrogen-1 NMR spectra (360 MHz) of the diastereoisomeric mixture **4a,4b**: (a, top) C_6D_6 solution; (b, middle) spectrum after addition of MeI (slight molar excess); (c, bottom) spectrum immediately after dissolution in a solution of MeI in C_6D_6. Note the change from *ca.* 60:40 intensity ratios (top, middle) to almost equal (bottom) (see text).

Scheme 1

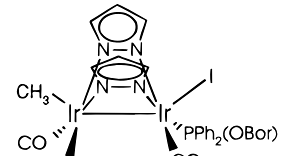


was removed and the residue was taken up in a minimum of THF; addition of petroleum ether reprecipitated the product, which after being washed thoroughly with pentane was isolated as a light orange powder, found[10] to be a mixture in a 60:40 ratio (^{1}H NMR: see Figure 1a) of the two diastereoisomers [Ir(P{OR*}Ph$_2$)(CO)(μ-pz)]$_2$ (R* = Bor, **4a,b**). The congeneric complexes **5a,b** (R* = Men) and **6a,b** were recovered from parallel experiments using menthyl diphenylphosphinite or dimenthyl phenylphosphonite,[9] P(OMen)$_x$Ph$_{3-x}$ (x = 1 or 2). The ^{31}P NMR spectrum of **4a,b** consists of two singlets at δ 93.6 and 95.1 ppm (*ca.* 63:37 ratio); in the ^{1}H NMR (illustrated in Figure 1a, C_6D_6), resonances assigned to H$^{5,5'}$, H$^{3,3'}$, and H$^{4,4'}$ of the μ-pz ligands and to the H^{C2-exo} protons are clearly distinguishable from those due to Ph and other bornyl hydrogens, at δ 7.48, 7.01, 5.80, and 5.63 (CD_2Cl_2, major diastereomer), 7.50, 6.99, 5.82, and 5.47 (minor). Attempted diastereomer separation by crystallization (THF) led to slow deposition of lustrous, regular, deep orange blocks that to our surprise consisted of *both* diastereomers, in a 50:50 ratio (NMR): this material therefore acts as a fortuitous supply of **4a,b** in *nonequilibrium distribution*, so that on dissolution in C_6D_6, the diastereomer ratio can be followed from almost equimolar to equilibrium (K = 1.5; *cf.* Figure 1a) over 60 min, giving $k_1 = 5.3 \times 10^{-4}$ s^{-1}, $k_{-1} = 3.5 \times 10^{-4}$ s^{-1}, and $\Delta G°_{298}$ = *ca.* 1.0 kJ mol^{-1}. An X-ray crystal structure determination, which confirmed the presence in the unit cell of both[11] diastereomers of **4**, converged to R = 0.0539 with maximum shift/σ = 0.177 after valid constraints on bornyl geometry were included to distinguish between diastereomeric dimers that lie almost parallel to one another in the structure, *i.e.* in a pseudosymmetric relationship. Crystal data for **4** and details of the refinement process are included in the Supporting Information; ORTEP plots for both molecules are shown in Figure 2, the caption to which provides selected bond distances and angles. The diastereomers, which possess identical stereochemistry for the bornyl fragments as is required but differ in the sense of rotation about the molecular C_2 axis (Figure 2), are otherwise similar in structure to the related atropisomeric analogue[12] [Ir(P{OC$_6$H$_4$Me}Ph$_2$)(CO)(μ-pz)]$_2$.



4a,b

The effect of addition of methyl iodide to a solution in benzene-d_6 of **4a,b** is shown in Figure 1. The ^{1}H NMR spectrum of the equilibrium mixture (Figure 1a) is replaced (Figure 1b) by superimposed spectra of the two diastereomeric MeI adducts[13] **7a,b**, formed in unchanged (60:40) distribution; these products are easily recognizable because the unsymmetrical substitution along the Ir$_2$ axis that gives **7a,b** lifts degeneracies among the μ-pz hydrogen pairs.[7,8] Thus, four signals due to H^{4,4a} are obvious near δ 5.5, while two of the H^{3,3a} family (δ 6.46, 6.28) clear the solvent peak and the H^{5,5a} group is partly overlapped to high frequency



7a,b

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[10] Anal. Found: C, 49.58; H, 4.79; N, 4.58. Calcd for $C_{52}H_{60}Ir_2N_4O_4P_2$: C, 49.91; H, 4.83; N, 4.48. IR/cm^{-1} (KBr): 1972 vs, 1965 vs.

[11] We are unaware of similar coexistence of diastereomers in any other crystal structure; see: Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1475.

[12] Farid, R. S.; Henling, L. M.; Gray, H. B. *Acta Crystallogr.* **1993**, *C49*, 1363.

[13] These can be isolated as an orange-yellow solid mixture, **7a,b**. Anal. Found: C, 45.32; H, 4.49; N, 3.97. Calcd for $C_{53}H_{63}IIr_2N_4O_4P_2$: C, 45.66; H, 4.52; N, 4.02. A weak parent ion was observed in the MS centered at m/z 1394 accompanied by stronger ion families due to CH_3 or I loss. IR/cm^{-1} (KBr): 2017 vs, 1983 vs.

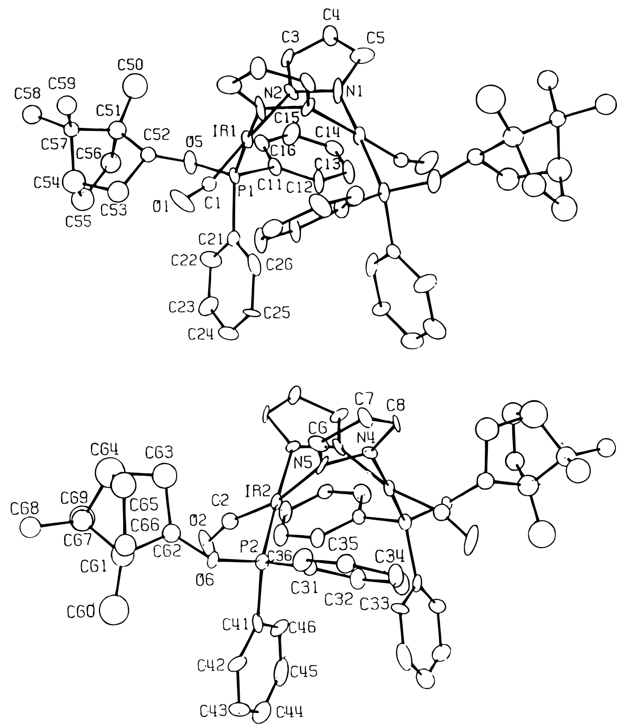

Figure 2. Molecular geometry of complex **4**: (top) molecule A; (bottom) molecule B. Selected bond distances (Å) and angles (deg): Ir(1)−Ir(1′) = 3.296(3), Ir(2)−Ir(2′) = 3.323(3), Ir(1)−P(1) = 2.227(6), Ir(2)−P(2) = 2.231(5), Ir(1)−N(1′) = 1.95(1), Ir(1)−N(2) = 2.06(1), Ir(2)−N(5) = 2.02(1), Ir(2)−N(4′) = 2.13(1), Ir(1)−C(1) = 1.88(2), Ir(2)−C(2) = 1.79(2); C(1)−Ir(1)−P(1) = 89.4(7), C(2)−Ir(2)−P(2) = 93.6(8), N(2)−Ir(1)−P(1) = 93.9(4), N(5)−Ir(2)−P(2) = 92.4(4), N(1′)−Ir(1)−N(2) = 87.7(9), N(4′)−Ir(2)−N(5) = 85.1(9).

(*i.e.* low field) of the latter. Two doublets, δ 1.70 (^2J = 1.89 Hz) and 1.74 (^2J = 1.73), are attributable to methyl hydrogens of major and minor adducts, respectively; a pronounced shift to low frequency (high field) of H^{C2-exo} is evident, toward the position characteristic of free P(OBor)Ph_2. Figure 1c depicts the ^{1}H NMR recorded immediately after addition of solid, crystalline **4a,b** to a premixed solution of MeI in C_6D_6; the spectra of the adducts **7a,b** are again visible but are now in equal ratio. Finally, very slow adjustment of the **7a,b** distribution is observed over 10 days at ambient temperature, leading to a ratio of 40:60 (K = 1.5) via apparent first-order behavior, with $k_{\mathbf{7a,b}} = 2.1 \times 10^{-6}$ s^{-1} and $k_{-\mathbf{7a,b}} = 1.4 \times 10^{-6}$ s^{-1}. Progress toward this inverted equilibrium distribution (*vs* that of **4a**−**4b**) was shut down by excess MeI (*ca.* 10 mol equiv); under these conditions there was no change in the ^{1}H NMR spectrum (Figure 1b) after 10 days.

These observations seem to us to be of fundamental interest for a number of reasons. Determination of the rate of ring inversion in a metallacyclic unit like that in **4a,b** is itself unprecedented. Interception of the nonequilibrium diastereomer distribution **4a**−**4b** by addition of MeI (yielding **7a,b**) establishes that oxidative addition is fast compared with the rate of core ring inversion. Since core disruption (either single bridge cleavage followed by rotation or dissociation to mononuclear fragments) will interconvert **4a,b**, it cannot be a part of the oxidative-addition process; the latter is identifiable for the first time as an unequivocally bimetallic event. Inhibition by excess MeI of the change in the kinetic diastereomer ratio **7a**:**7b** implies that reductive elimination (*i.e.* of MeI, the reverse of **7a,b** formation from **4a,b**) is mechanistically significant in the observed slow shift away from the **4a,b** equilibrium distribution. Conditions under which related systems might function with greater kinetic discrimination to act as selective catalysts are being sought.

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Supporting Information Available: Text providing crystal data for complex **4a,b** and a description of how the structure was solved, together with tables of fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, interatomic distances, bond angles, and selected intermolecular distances (8 pages). Ordering information is given on any current masthead page.

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