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Highly Diastereoselective Oxidative Addition of Methyl Iodide to a Chiral Square-Planar Complex

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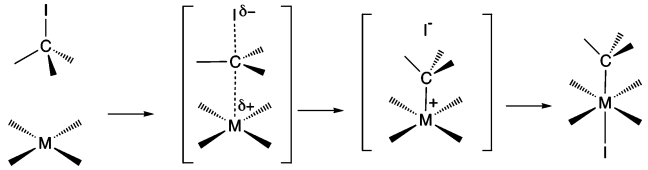
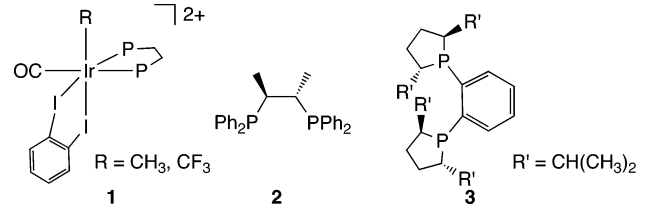
Oxidative addition of methyl iodide to the chiral square-planar complex IrI(CO)(duphos) shows a high level of diastereoselectivity. The basis for the diastereoselectivity of the reaction is best explained based on the crystal structure of IrI(CO)(duphos) in which methyl iodide approach across the two faces is differentiated by the chiral ligand.

Activation of small molecules via oxidative addition to electron-rich transition-metal complexes plays a central role in many catalytic processes.[1] A classical example is the addition of MeI to *cis*-$[MI_2(CO)_2]^-$ (M = Rh or Ir) in the industrial carbonylation of methanol to form acetic acid.[2−5] It is widely accepted that the oxidative addition of MeI to these square-planar d^8 metal complexes occurs via a two-step mechanism (Scheme 1) involving (i) nucleophilic attack by the d^8 metal ion on the methyl C to displace iodide via a linear three-center transition state to form a metal−carbon bond and (ii) addition of iodide to the resultant five-coordinate intermediate trans to the Me group.[6−8] While diastereoselective oxidative addition of MeI to a square-planar complex having a chiral ligand is indeed possible, to the best of our knowledge no such diastereoselectivity in this reaction has so far been reported. In this Communication, we describe such a reaction that proceeds with high diastereoselectivity to a chiral square-planar Ir^I complex. While results involving square-planar complexes are uncommon, high diastereoselectivity has been observed in MeI oxidative addition to the chiral, Cp-containing complexes [Rh(η^5-C_5H_4-$CH_2CH(Ph)PPh_2$-κP)(η^2-CH_2CH_2)] (93:7 ratio in THF)[9] and [Ir(η^5-$C_5H_4CH_2CH(Cy)PPh_2$-κP)(η^2-C_8H_{14})] (90:10 ratio in CH_2Cl_2),[10] but in neither case is a *square*-planar intermediate generated in the course of the reaction.

Scheme 1



Previously, we have reported the synthesis of [IrR(CO)(dppe)(DIB)]$(BAr^f_4)_2$ (**1**), where R = Me or CF_3, DIB = *o*-diiodobenzene, dppe = 1,2-bis(diphenylphosphino)ethane, and BAr^f_4 = B(3,5-$(CF_3)_2C_6H_3)_4$, via the corresponding $IrRI_2$(CO)(dppe) complex formed by RI oxidative addition to IrI(CO)(dppe).[11,12a] In **1**, the weakly chelating DIB ligand[12b] is labile enough for facile substitution and stable enough for isolation and storage of the Ir^{III} complex. Both complexes were found to function as cationic initiators for polymerization or oligomerization of electron-rich olefins and conjugated dienes,[11−13] and in recent reports, we have investigated **1** as a highly efficient, well-defined catalyst for promoting the Nazarov reaction.[14−20]



1 **2** **3**

For the purpose of generating chiral analogues of complex **1** for asymmetric catalysis, Ir^I precursor complexes contain-

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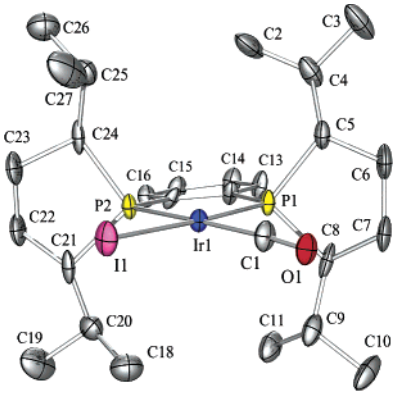


Figure 1. POVRAY representation of **5** showing 35% probability ellipsoids. For clarity, H atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir1−C1, 1.877(7); Ir1−P1, 2.2419(11); Ir1−P2, 2.3092(12); C1−Ir1−P2, 175.7(3); C1−Ir1−I1, 90.4(2); P1−Ir1−I1, 177.63(7).

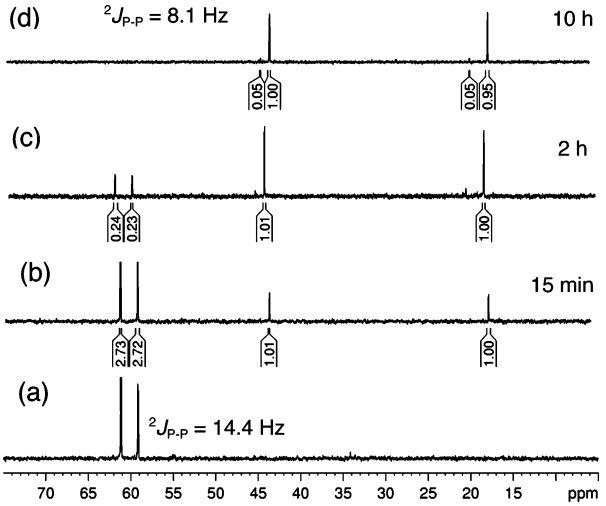
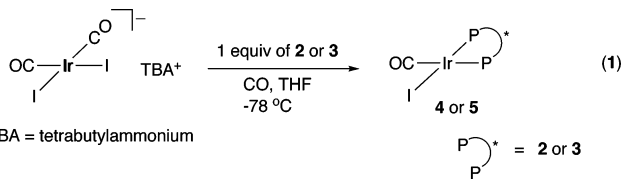


Figure 2. $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 at room temperature of (a) **5**, (b) **5** plus MeI after 15 min of mixing, (c) **5** plus MeI after 2 h of mixing, and (d) **5** plus MeI after 10 h of mixing.

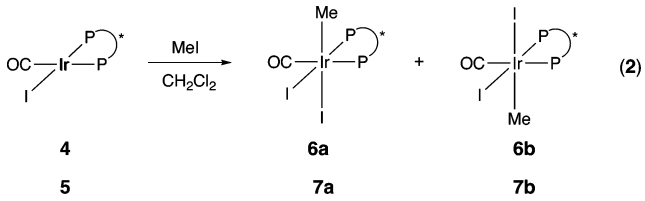
ing enantiopure diphosphine ligands 2,3-bis(diphenylphosphino)butane (chiraphos, **2**) and 1,2-bis(2,5-diisopropylphospholano)benzene (duphos, **3**) were synthesized by the reaction of 1 equiv of **2** or **3** with $[IrI_2(CO)_2]^-$ at low temperature to yield respectively **4** or **5** in good yield (eq 1).[21]



(1)

The complexes were characterized by NMR and IR spectroscopies and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum of chiraphos complex **4** exhibits a pair of doublets at δ 48.2 and 44.5 (each with $^2J_{PP}$ = 25.0 Hz) in CD_2Cl_2 corresponding to the inequivalent *cis*-phosphine donors. Similarly, for duphos complex **5**, the $^{31}P\{^1H\}$ spectrum shows a pair of doublets at δ 61.1 ($^2J_{PP}$ = 14.4 Hz) and 59.1 ($^2J_{PP}$ = 14.4 Hz) in CD_2Cl_2 (Figure 2a). The structure of **5**, determined crystallographically (see the Supporting Information) and shown in Figure 1, consists of a square-planar coordinated Ir^I ion with disordered CO and iodide ligands (76:24) and a nearly C_2-symmetric duphos ligand having the arene backbone in the IrP_2 plane. Disorder that exists in the substituents of one of the duphos phospholane rings has been successfully modeled (53:47).

The reaction of chiraphos complex **4** with MeI in CH_2Cl_2 at room temperature affords the two diastereomers **6a** and **6b** in a 50:50 ratio, resulting from chirality at both the Ir center and the chiraphos ligand **2** (eq 2). The fact that a 50:



(2)

50 mixture of diastereomers is obtained indicates that the two diastereotopic faces of the Ir^I precursor complex are sterically similar. When this reaction is followed by ^{31}P NMR spectroscopy, it is complete in less than 15 min, analogous to the oxidative addition of MeI to the achiral complex IrI(CO)(dppe).[22] The IR spectrum of the diastereomeric products **6a** and **6b** displays an intense ν(CO) absorption at 2056 cm^{-1}, consistent with an Ir^{III} complex having a terminal CO ligand.

In contrast to the reaction with **4**, the oxidative addition of MeI to the more sterically crowded duphos complex **5** requires several hours for completion, as shown in Figure 2b−d. In this reaction, a great surprise was provided by a 95:5 diastereomeric ratio (90% de) of the Ir^{III} duphos product **7**. The diastereomers **7a** and **7b** were characterized by NMR and IR spectroscopies, as well as X-ray crystallography for the major isomer.

An ORTEP representation of the major isomer of **7**[23] with selected bond lengths and angles is shown in Figure 3 (see the Supporting Information for details). The complex displays a distorted octahedral geometry around Ir. The different Ir−P bond lengths of 2.2854(6) and 2.3762(6) Å are consistent with the trans structural influence of iodide and CO, respectively, and are similar to those of complex **5**. While the Ir−C2 bond length of 2.127(3) Å is similar to the 2.12(2) Å value observed for the $[Ir(Me)I_2(CO)(dppe)]$ complex,[22] it must be noted that there exists an occupational disorder between methyl carbon C2 and iodide ligand I2, with the

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(23) $^{31}P\{^1H\}$ NMR recorded for the crystal on which the X-ray data were collected showed that it is the major isomer.

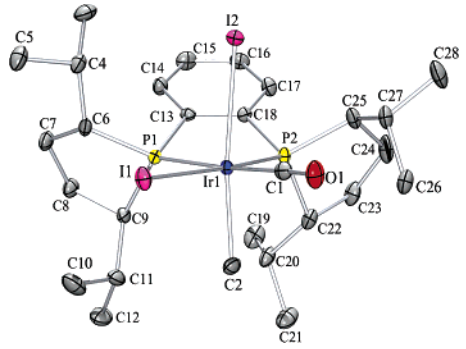


Figure 3. POVRAY representation of the major isomer of **7** showing 50% probability ellipsoids. For clarity, H atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir1−C1, 1.909(3); Ir1−C2, 2.127(3); Ir1−P2, 2.2854(6); Ir1−P1, 2.3762(6); C1−Ir1−C2, 85.98(11); C2−Ir1−P2, 94.77(9); C1−Ir1−P1, 173.22(8); C2−Ir1−P1, 98.03(9); P2−Ir1−P1, 83.66(2); C2−Ir1−I1, 87.56(9); P2−Ir1−I1, 175.499(17).

latter occupying the methyl C position in the coordination sphere 3% of the time (occupation of the I2 position by the methyl C with an occupancy factor of 0.03 cannot really be discerned crystallographically).

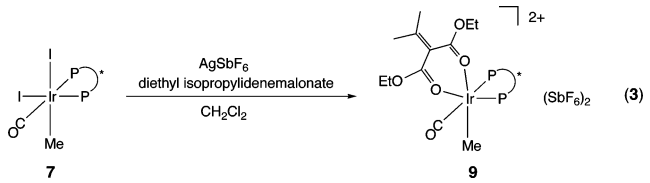
In contrast with the structure of **5**, the duphos backbone and phenylene ring of **7** deviate from the IrP_2 plane with a dihedral angle of 29° (see the Supporting Information for ORTEP figures). The C_2 symmetry of the chiral ligand that is evident in **5** is clearly missing in **7**. On the basis of the fact that the phenylene ring of the duphos ligand is tilted away from the Me and toward the bulkier trans iodide ligand, we suggest that the initial methylation step leads to the dramatic change in the Ir duphos chelate ring conformation.

The diastereoselectivity of the MeI addition to **5** appears at first analysis to be inconsistent with one aspect of the mechanism shown in Scheme 1, namely, the linear nature of the Ir···CH_3···I transition state in the methylation step, because this would appear to be the same from above and below the plane of **5**, suggesting no diastereoselectivity in the step. The polar nature of the reaction was probed by solvent and medium variation in order to provide further insight into the reaction mechanism. In more polar DMSO-d_6, MeI addition to **5** proceeded at least one order of magnitude faster than that in CD_2Cl_2, while in less polar toluene-d_8, the addition was ~75% slower, but in each case the diastereoselectivity remained essentially unchanged. Additionally, the rate of MeI addition in the presence of 6 equiv of iodide increased by a factor of two, but again there was no change in the diastereoselectivity. While the results do not conclusively rule out diastereoselection after the methylation step, they appear inconsistent with the notion that the five-coordinate Ir−Me intermediate could consist of an equilibrium mixture because diastereoselective trapping with iodide would be affected by solvent polarity.

A closer examination of the steric constraints of the **5** + MeI reaction system does, in fact, offer guidance regarding the basis of the diastereoselectivity. To aid in this study, the C_2-symmetric complex $[Ir(CO)_2(duphos)][SbF_6]$ (**8**) was synthesized and crystallographically characterized. This complex, which was prepared by adding $AgSbF_6$ to a solution of **5** under CO, exhibits a square-planar structure with the phenylene ring of the duphos ligand coplanar with the plane defined by Ir and the two P donors. Complex **8** avoids the CO/I disorder seen for **5** with the resultant disorder in the substituents of one of its phospholane rings (see the Supporting Information for ORTEP and space-filling representations of **8**).

While the C_2 symmetry of **8** indicates that methylation of the complex following a linear Ir···CH_3···I transition state should be energetically equivalent from either side of the coordination plane, an activation energy difference will exist *if* the Ir···CH_3···I transition state deviates from linearity along a specific projection on the complex plane. Thus, the addition of MeI with its molecular axis in the same plane as a particular P−Ir−CO axis of **8** will differ energetically in approaches from above and below the metal complex plane. The structure of **8** further supports this notion because of steric interactions akin to a "gearing" effect that exists between isopropyl groups on different phospholane rings. In the case of **5** with only one P−Ir−CO axis (and one P−Ir−I axis), the approach of MeI along a specific axis of **5** from either side of the coordination plane will therefore have different activation energies, thus explaining the observed diastereoselectivity.

Once established, the chirality at Ir appears to be preserved. We have previously reported that the iodide ligands in $IrMeI_2$-(CO)(dppe) can be removed using $AgSbF_6$, and in the presence of diethyl isopropylidenemalonate, another Ir^{III} complex with a readily dissociable chelating ligand can be formed and structurally characterized.[20] This same reaction when repeated with **7** by the addition of 2 equiv of $AgSbF_6$ and 1 equiv of diethyl isopropylidenemalonate in CH_2Cl_2 leads to the formation of two diastereomers of **9** in a 94:6 ratio that is essentially indistinguishable from the ratio of diastereomers found for **7** (eq 3). The $^{31}P\{^1H\}$ NMR spectrum of the major dicationic complex **9** exhibits a pair of doublets at δ 49.4 ($^2J_{PP}$ = 3.3 Hz) and 38.0 ($^2J_{PP}$ = 3.3 Hz) in CD_2Cl_2, while the minor isomer displays resonances at δ 48.0 and 37.7.



7 **9** (3)

In conclusion, we have shown that, by employment of sterically encumbered chiral duphos ligand **3**, it is possible to attain a highly diastereoselective oxidative addition of MeI to an Ir^I precursor complex. Asymmetric catalysis studies using the dicationic complex **9** are underway and will be reported in due course.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental details for the synthesis and characterization of **4**−**9**, tables of unit cell, data collection, and refinement parameters for each structure determination, ORTEP diagrams for **5** and **8**, and a space-filling diagram for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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