complex and rearrangement to a π-allyl complex. The detailed mechanism of these rearrangements as well as the chemistry of other substituted Fp-cyclopropyl complexes is currently under investigation.

Acknowledgment. We are grateful to the National Science Foundation for its support of this work.

Regioselective Chelate Assisted Carbon-Halogen Oxidative Addition at Tungsten(0)

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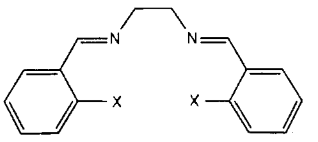
Summary: Regioselective aromatic carbon-halogen oxidative addition is observed in unsymmetrically substituted chelating ligands derived from 1,2-diaminobenzene. Aromatic carbon-chloride bonds on an imine arm of the ligand are cleaved in the presence of aromatic carbon-iodine bonds on a saturated arm. Crystallographic and vibrational analyses show that hydrogen bonding is important in the structure of the seven-coordinate tungsten(II) metallacycle product.

An important mode of activation and potential catalytic functionalization of carbon-heteroatom bonds is by oxidative addition to a low-valent metal.[1] Recently we reported that cleavage of aromatic carbon-halogen bonds in suitably designed ligands (**1**, X = Cl, Br, I) takes place readily at tungsten(0).[2] Interestingly, oxidative addition was not observed for the closely related conjugated ligand system **2**. The basis for the diverse reactivity observed for chelates **1** and **2** may be a result of differing metal basicity[3] rather than ligand structure. In order to probe the role of the ligand in promoting these reactions, we have prepared several unsymmetrical ligands to compare the reactivity of saturated versus unsaturated pendant aryl halides to oxidative addition at an identical metal center. Mechanistic understanding of this type of reaction is important in the design of ligands for specific bond activation reactions at metal centers.[4]



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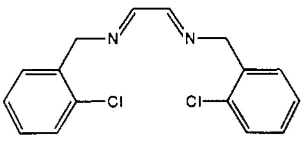


2

Reduction of the 1:1 Schiff base **3** prepared from 1,2-diaminobenzene and a substituted benzaldehyde followed by treatment with 1 equiv of 2,6-dichlorobenzaldehyde affords **4a** and **4b** in approximately 70% yield (see Scheme I).[6] Treatment of **4** with W(CO)$_3$(EtCN)$_3$[5] in dichloromethane at room temperature for 2 h yields reddish orange solutions of **5a** and **5b** which can be isolated as orange crystalline solids in 70% and 63% yields, respectively.

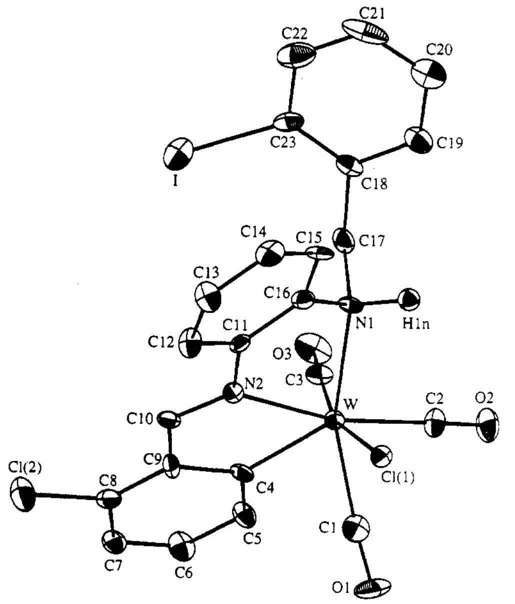
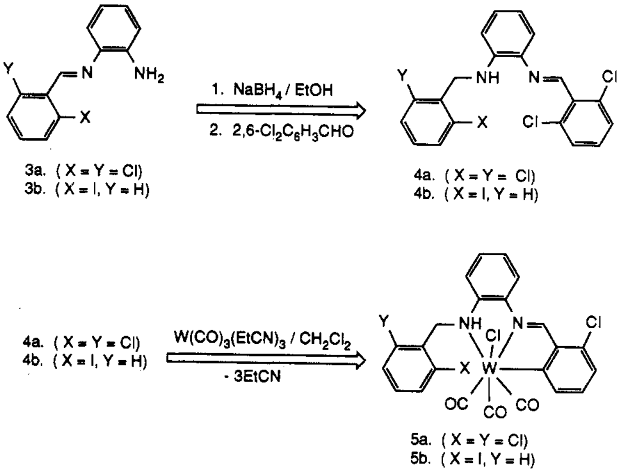


Figure 1. ORTEP representation of **5b**. Selected bond distances (Å) are as follows: W-C4, 2.20 (1); W-Cl(1), 2.536 (1); W-N1, 2.314 (7); W-N2, 2.154 (8); W-Cl, 2.03 (1); W-C2, 2.01 (1); W-C3, 1.97 (1). Selected bond angles (deg) are as follows: N1-W-Cl(1), 79.3 (2); N2-W-Cl(1), 84.1 (2); C4-W-Cl(1), 125.7 (2); N1-W-Cl, 155.3 (4); N2-W-C2, 167.7 (4); Cl(1)-W-C3, 165.6 (3).

Scheme I



These compounds were characterized by elemental analysis and ^{1}H NMR and IR spectroscopic methods. In the case of **5a**,[7] the imine proton at δ 9.953 exhibits distinct satellites ($^3J_{WH}$ = 8.4 Hz) due to coupling to ^{183}W. This coupling is diagnostic of metallacycle formation in structurally characterized complexes of related ligands.[2,4] A broad resonance at δ 5.78 assigned to the N-H group is coupled to the diastereotopic protons of the benzyl arm

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(6) Analytical data for **4a**: IR (mull, cm^{-1}) 3348 (ν_{NH}), 2477 (ν_{ND}); ^{1}H NMR (CDCl$_3$) δ 8.803 (s, 1 H, HC=N), 7.4-6.7 (m, 10 H, aromatic), 5.49 (br, 1 H, NH), 4.66 (s, 2 H, CH$_2$). Anal. Calcd for $\mathrm{C_{20}H_{14}N_2Cl_4}$: C, 56.77; H, 3.10; N, 6.62. Found: C, 56.81; H, 3.28; N, 6.58. Spectral data for **4b**: IR (mull, cm^{-1}) 3377 (ν_{NH}); ^{1}H NMR (CDCl$_3$) δ 8.874 (s, 1 H, HC=N), 7.8-7.1 (m, 11 H, aromatic), 4.37 (br, 1 H, NH), 4.17 (d, ^3J = 2.7 Hz, 2 H, CH$_2$).

(7) Anal. Calcd for $\mathrm{C_{23}H_{14}N_2Cl_4O_3W}$ (**5a**): C, 36.93; H, 1.89; N, 3.74. Found: C, 37.12; H, 2.13; C, 3.67.

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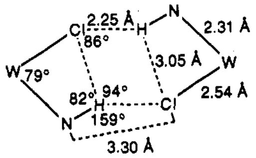
of the ligand (δ 5.092 (dd, $^3J_{HH}$ = 2.6 Hz, $^2J_{HH}$ = 13.8 Hz, 1 H), 4.438 (dd, $^3J_{HH}$ = 10.7 Hz, $^2J_{HH}$ = 13.8 Hz, 1 H). Addition of D_2O results in rapid exchange of the amine proton and loss of coupling to the benzylic hydrogens. The N–H stretch appears at 3255 cm^{-1} and the N–D stretch for the deuteriated material, prepared by exchange with excess D_2O in THF, occurs at 2422 cm^{-1}. Strong metal carbonyl bands observed at 2021, 1946, and 1905 cm^{-1} in CH_2Cl_2 are consistent with the tungsten(II) metallacycle formulation.[2,4]

Spectral properties of **5b** are similar,[8] and the regiochemistry of the product was confirmed by X-ray diffraction analysis of single crystals obtained from CH_2Cl_2/hexanes (Figure 1).[9] The seven-coordinate tungsten(II) metallacycle is formed by oxidative addition at the carbon–chlorine bond on the imine arm of the ligand. The geometry about tungsten can be approximated as a capped octahedron with the phenyl group as the cap.[2] The carbon–iodine bond remains intact. Direct ^{1}H NMR analysis of the crude reaction mixture failed to detect any other isomeric product. Thus the asymmetry of the ligand results in activation of the stronger C–Cl bond (95 kcal/mol) in the presence of a weaker C–I bond (64 kcal/mol).[10] This result implies that the unsaturated imine arm of the ligand is crucial in promoting oxidative addition to tungsten(0). Both steric (restricted rotation about the C═N bond) and electronic (conjugation of the C═N bond with the phenyl ring) factors appear to promote the oxidative addition process.

Structural studies of **5b** reveal that both intra- and intermolecular hydrogen bonding takes place between the chloride coordinated to tungsten (Cl(1)) and the proton of the amine group (H1n). Unfortunately, H1n could not be unambiguously located on the final electron density difference map and was placed in the calculated position. Intermolecular hydrogen bonds occur between pairs of molecules related by a center of inversion; metrical parameters are given below.



Both intramolecular N1···Cl (2.97 Å) and intermolecular N1···Cl (3.30 Å) are in the range expected for hydrogen bonding.[11] The close intramolecular N1···Cl interaction is in part a consequence of the acute N1–W–Cl angle of 79.3 (2)° in this seven-coordinate complex. The intermolecular N–H···Cl angle is much closer to 180° than the intramolecular case resulting in a significantly shorter H···Cl distance.[12] The importance of these intermolecular hydrogen bonds is seen in the solid state packing of this molecule. However, solution molecular weight measurements (Signer isothermal distillation)[13] on **5a** indicate that it is monomeric in dichloromethane. The observed ν_{NH}/ν_{ND} ratio of 1.34 is smaller than that expected (1.36) for molecules where hydrogen bonding is unimportant.[14]

The structural chemistry of this molecule provides a contrast to the behavior of a series of six-coordinate Rh(III) and Ir(III) amino halides in which intramolecular hydrogen bonding appears to be more important than intermolecular interactions.[15] Further exploration of ligand-based control of bond activation reactions and the role of hydrogen bonding in the chemistry of these materials is in progress.[16]

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Supplementary Material Available: Full crystallographic data for **5b** including tables of bond distances and angles and final positional and thermal parameters (16 pages); a listing of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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(8) Analytical data for **5b**: IR (CH_2Cl_2, cm^{-1}) 3226 (w, ν_{NH}), 2404 (w, ν_{ND}), 2020 (s), 1944 (s), 1906 (s) (ν_{CO}); nonaromatic ^{1}H NMR (acetone-d_6) δ 9.877 (s, 1 H, HC═N, $^3J_{WH}$ = 8.5 Hz), 6.304 (dd, ^3J = 10.7, 3.7 Hz, 1 H, NH), 5.027 (dd, ^2J = 13.4, ^3J = 3.7 Hz, 1 H, C*H*H′), 4.222 (dd, ^2J = 13.4, ^3J = 10.7 Hz, 1 H, CH*H*′). Anal. Calcd for $C_{23}H_{15}N_2Cl_2IO_3W$: C, 36.88; H, 2.02; N, 3.74. Found: C, 36.70; H, 2.06; C, 3.72.

(9) Crystal data for **5b**: $WICl_2O_3N_2C_{23}H_{15}$, red-orange, monoclinic, $P2_1/a$, a = 11.239 (4) Å, b = 15.533 (8) Å, c = 14.296 (4) Å, β = 106.60 (3)°; V = 2391.7 Å^3, Z = 4, Mo Kα. Of 4155 reflections collected at ambient temperature (Syntex P$\bar{1}$, 3° < 2θ < 48°) 3721 were unique of which 2386 had $I > 3\sigma(I)$ and were used in the solution and refinement (SDP PLUS Software). Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. For 289 parameters, R = 0.039 and R_w = 0.043, GOF = 1.7, and highest peak in the final map of 1.1 e/Å^3 approximately 0.99 Å from W.

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Reversal of Stereochemical Path in Allylic Alkylations Promoted by Palladium and Molybdenum Complexes

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Summary: In allylic alkylations using palladium complexes, the oxidative addition of an allyl acetate to the metal usually occurs with inversion of configuration. The addition of (+)-(*R*)-(*E*)-4-acetoxy-5-methyl-2-hexene to $(CH_3CN)_3Mo(CO)_3$ has been shown to occur with retention of configuration. This leads to a reversal of the chirality at the stereogenic center formed in the addition of nucleophiles, such as malonate, when the products of palladium-catalyzed reactions are compared to those from stoichiometric reactions on molybdenum complexes. These results suggest that whereas net retention is a consequence of double inversion in the palladium-catalyzed reactions, net retention is a consequence of double retention in many molybdenum-catalyzed reactions of this type.

We have demonstrated the utility of cationic [CpMo(NO)(CO)(η^3-allyl)]$^+$ complexes in stoichiometric asym-

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