Molybdenum η^2-imine complex formation and the reductive coupling of imines†

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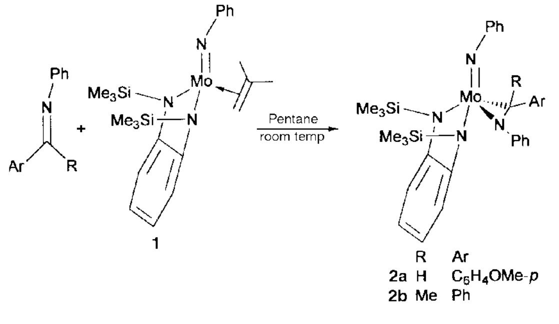
Received (in Bloomington, IN, USA) 5th January 2000, Accepted 25th February 2000
Published on the Web 17th March 2000

Addition of imine PhN=C(Ar)R (Ar = Ph, R = Me; *p*-MeOC$_6$H$_4$, R = H) to (PhN)Mo(TMS-*o*-pda)(CH$_2$=CMe$_2$) 1 [TMS-*o*-pda = bis(trimethylsilyl)-*o*-phenylenediamide] affords the corresponding η^2-imine complexes (PhN)Mo(TMS-*o*-pda)[PhN=C(Ar)R] 2a and 2b; analogous reactions with aldimines RN=C(H)Ar (Ar = *p*-MeOC$_6$H$_4$, R = CH$_2$Ph, Et) afford products (PhN)Mo(TMS-*o*-pda)-[RNC(H)ArC(H)ArNR] 3a and 3b resulting from reductive imine coupling, providing the first example of facile and general Mo(IV) η^2-imine complex formation.

Current synthetic methodologies affording η^2-imine complexes (azametallacyclopropanes) consist of C–H activation from methylmetallocene amides,[1,2] rearrangements of iminoacyl complexes,[3] reaction between Cp$^*{}_2$ZrH$_2$ and ArNC,[4] reduction of a low-valent complex with phosphaazaallene,[5] and various *in situ* methods of η^2-imine complex formation.[6] Isolation and characterization of η^2-imine complexes generated by direct reaction of imines with metal reductants has for the most part been unsuccessful, and although two recent reports detail the isolation and characterization of ytterbium[6] and tantalum[7] η^2-imine complexes *via* such direct methods, examples with other early transition metals are, to our knowledge, non-existent. We report herein structural characterization and direct synthesis of molybdenum(IV) η^2-imine complexes obtained by treatment of the molybdenum(IV) olefin complex (PhN)Mo(TMS-*o*-pda)(CH$_2$=CMe$_2$) **1**[8] with appropriate aldimines and ketimines. Furthermore, aldimine reductive coupling products are isolated for less sterically demanding aldimines.

Reaction of the aryl amine derived aldimine PhN=C(H)Ar or ketimine PhN=C(Me)Ph with **1** affords the η^2-imine complexes **2a** and **2b**, respectively, as green crystals in 70% isolated yield (Scheme 1).‡ The molecular structure of **2b** was determined by an X-ray crystallographic study, and selected bond distances and angles for **2b** are shown in Fig. 1.§

Complex **2b** adopts a five-coordinate square pyramidal geometry with the imido ligand occupying the apical position. The short imido Mo(1)–N(3) bond length of 1.736(2) Å is typical of a Mo–N triple bond interaction.[9] The Mo(1)–N(4), Mo(1)–N(2) and Mo(1)–N(1) bond lengths of 1.944(2), 2.009(2) and 1.996(2) Å, respectively, are all consistent with Mo–N single bonds.[10] The C(31)-centered bond angles of the imine fragment are all < 120° and support a considerable amount of azametallacyclopropane character in **2b** as does the N(4)–C(31) bond length of 1.414(3) Å.[11]



Scheme 1 The generation of molybdenum(IV) η^2-imine complexes.

Complete conversion of **2a** to the corresponding organic amine (PhNHCH$_2$Ar) was observed by ^{1}H NMR upon exposure of a solution of **2a** to an atmosphere of 15 psi H$_2$ at room temperature over a 1 week period.[12] Unfortunately no catalytic activity was observed upon treatment of **2a** with excess imine under low pressures (*ca.* 15 psi) of H$_2$ gas.

The reaction of aldimines derived from less hindered primary amines with **1** affords molybdenum(VI) bisdiamide imido complexes **3a** and **3b** from reductive imine coupling (Scheme 2).‡ Complexes **3a** and **3b** were isolated in 75% yield from cold pentane–toluene solutions. Interestingly, only the *rac*-coupled form of the metal complexes is isolated as ascertained from ^{1}H and ^{13}C NMR spectroscopy. An X-ray crystallographic study was performed on a single crystal of **3b**.

The molecular structure and selected bond lengths and angles are shown in Fig. 2.§ The complex adopts a distorted square pyramidal geometry around molybdenum with the imido ligand

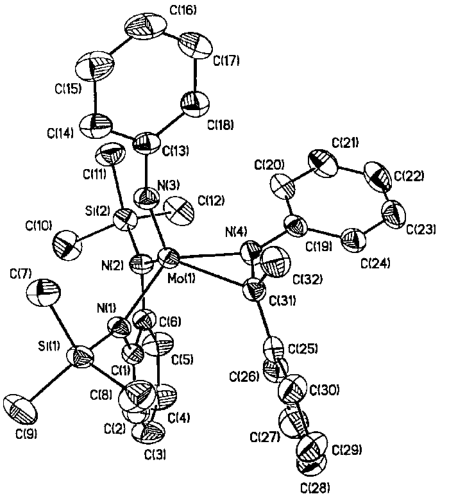


Fig. 1 Thermal ellipsoid plot of **2b**. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.996(2), Mo(1)–N(2) 2.009(2), Mo(1)–N(3) 1.736(2), Mo(1)–N(4) 1.944(2), Mo(1)–C(31) 2.200(3), N(3)–C(13) 1.409(3), N(4)–C(31) 1.414(3), C(31)–C(32) 1.518(4); Mo(1)–N(3)–C(13) 163.0(2), N(2)–Mo(1)–N(1) 85.28(9), N(4)–Mo(1)–C(31) 39.29(9), N(2)–Mo(1)–N(4) 100.09(9), N(1)–Mo(1)–C(31) 99.20(9), N(4)–C(31)–Mo(1) 60.55(13), N(4)–C(31)–C(32) 116.9(2), N(4)–C(31)–C(25) 116.6(2), C(32)–C(31)–C(25) 116.2(2).

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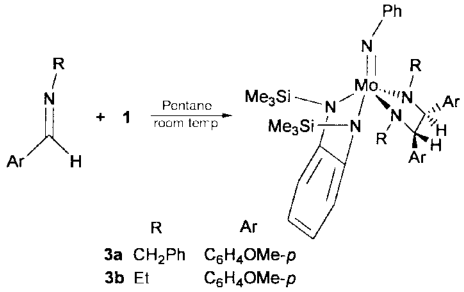
† Electronic supplementary information (ESI) available: spectroscopic data for **1**, **2a**, **2b**, **3a** and **3b**. See http://www.rsc.org/suppdata/cc/b0/b000355g/

DOI: 10.1039/b000355g



Scheme 2 The reductive coupling of imines.

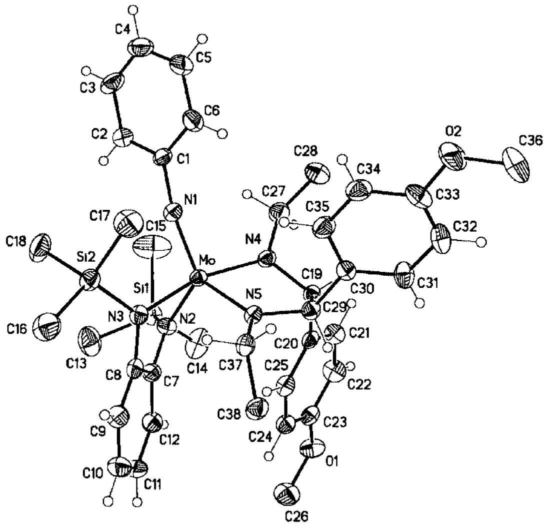


Fig. 2 Thermal ellipsoid plot of **3b** with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Mo–N(1) 1.754(3), Mo–N(2) 2.008(3), Mo–N(3) 2.065(3), Mo–N(4) 1.996(3), Mo–N(5) 2.021(3), N(4)–C(19) 1.476(5), N(5)–C(29) 1.468(5), C(19)–C(29) 1.514(5); Mo–N(1)–C(1) 166.6(3), N(2)–Mo–N(3) 80.65(14), N(3)–Mo–N(5) 85.75(12), N(5)–Mo–N(4) 77.46(12), N(2)–Mo–N(4) 102.59(12).

occupying the apical position. The Mo–N(1) bond length of 1.754(3) Å is consistent with a molybdenum nitrogen triple bond interaction.[9] The Mo–N(2), N(3), N(4) and N(5) amide bond lengths of 2.008(3), 2.065(3), 1.996(3) and 2.021(3) Å, respectively, are within the range expected for Mo–N single bonds.[10] The hydrogen atoms located on the backbone of the newly formed diamide ligand are related by an H–C(19)–C(29)–H torsion angle of 90°. Consistent with this torsion angle there is no observed coupling between these protons in the solution ^{1}H NMR spectrum at 300 MHz. Complex **3a** displays similar characteristics in its ^{1}H NMR spectrum.

In summary, we have demonstrated that chelate-supported Mo(IV) η^2-imine complexes can be easily prepared *via* displacement of olefin from **1** upon reaction with *N*-aryl imines. In contrast, imine reductive coupling products were observed for sterically less demanding imines. We are currently investigating the reactivity of these η^2-imine complexes with unsaturated organic molecules.

J. M. B. thanks the National Science Foundation (CHE 9523279) for funding of this work. K. A. A. thanks the NSF and the University of Florida for funding X-ray equipment purchases, and R. T. B. thanks the Science and Technology Base programs at Los Alamos.

Notes and references

‡ All reactions and manipulations were carried out using standard Schlenk techniques or a dry box under atmospheres of nitrogen and argon. *Synthesis* of **2a** and **2b**: to a green solution of **1** (0.50 g, 1.05 mmol) in pentane at room temperature was added a pentane solution of the appropriate imine (0.20 g, 1.05 mmol). After stirring for 12 h the pentane solution was concentrated *in vacuo* and cooled, affording the appropriate metal complexes. The synthesis of **3a** and **3b** was similar but required the addition of 2 equivalents of the appropriate imine.

§ *Crystal data*: for **2b**: $C_{32}H_{40}N_4Si_2Mo$, M = 632.80, a = 9.8565(5), b = 18.8443(8), c = 17.9089(8) Å, β = 104.6520(1)°, V = 3218.2(3) Å^3, monoclinic, space group $P2_1/c$, Z = 4, T = 203(2) K, final $R1$ = 0.0431, $wR2$ = 0.0831, GOF (on F^2) = 1.225.

For **3b**: $C_{38}H_{53}MoN_5O_2Si_2$, M = 763.97, a = 9.9600(5), b = 19.0705(9), c = 10.2628(5) Å, β = 97.351(1)°, V = 1933.3(2) Å^3, monoclinic, space group $P2_1$, Z = 2, T = 173(2) K, final $R1$ = 0.0420, $wR2$ = 0.0775, GOF (on F^2) = 1.021.

Both structures were solved using the direct methods option of SHELXS. Full-matrix least-squares refinements based on F^2 were subsequently performed using SHELXL 97.[13] All non-hydrogen atoms were assigned anisotropic temperature factors, with corresponding hydrogen atoms included in calculated positions.

CCDC 182/1560. See http://www.rsc.org/suppdata/cc/b0/b000355g/ for crystallographic files in .cif format.

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Communication b000355g