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

Tom M. Cameron,[a] Carlos G. Ortiz,[a] Khalil A. Abboud,[a] James M. Boncella,*[a] R. Tom Baker[b] and Brian L. Scott[b]

[a] *Department of Chemistry, University of Florida, Gainesville, FL 32611, USA. E-mail: boncella@chem.ufl.edu*
[b] *Chemical Science and Technology Division, Los Alamos National Laboratory, MS J514, Los Alamos, NM 87545, USA*

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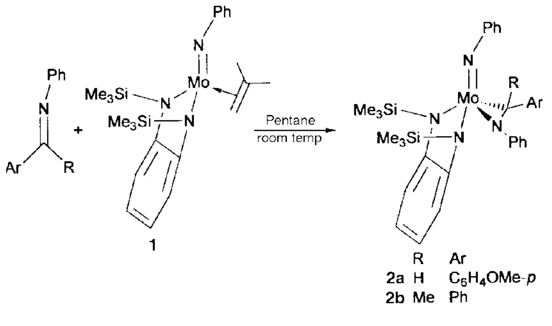
Addition of imine PhN=C(Ar)R (Ar = Ph, R = Me; *p*-MeOC$_6$H$_4$, R = H) to (PhN)Mo(TMS-*o*-pda)(CH$_2$=CMe$_2$) 1 [TMS-*o*-pda = bis(trimethylsilyl)-*o*-phenylenediamide] affords the corresponding η^2-imine complexes (PhN)Mo(TMS-*o*-pda)[PhN=C(Ar)R] 2a and 2b; analogous reactions with aldimines RN=C(H)Ar (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

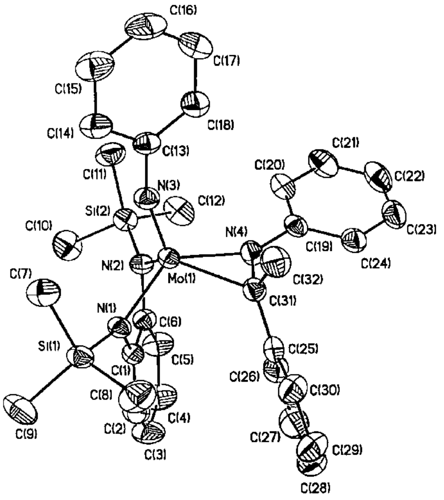


Fig. 1 Thermal ellipsoid plot of **2b**. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.996(2), Mo(1)–N(2) 2.009(2), Mo(1)–N(3) 1.736(2), Mo(1)–N(4) 1.944(2), Mo(1)–C(31) 2.200(3), N(3)–C(13) 1.409(3), N(4)–C(31) 1.414(3), C(31)–C(32) 1.518(4); Mo(1)–N(3)–C(13) 163.0(2), N(2)–Mo(1)–N(1) 85.28(9),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

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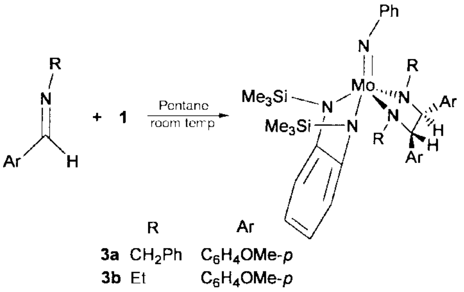

Scheme 2 The reductive coupling of imines.

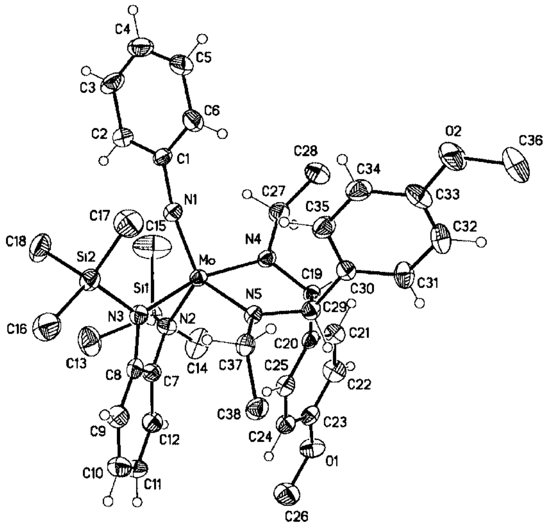

Fig. 2 Thermal ellipsoid plot of **3b** with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Mo–N(1) 1.754(3), Mo–N(2) 2.008(3), Mo–N(3) 2.065(3), Mo–N(4) 1.996(3), Mo–N(5) 2.021(3), N(4)–C(19) 1.476(5), N(5)–C(29) 1.468(5), C(19)–C(29) 1.514(5); Mo–N(1)–C(1) 166.6(3), N(2)–Mo–N(3) 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 ^1H NMR spectrum at 300 MHz. Complex **3a** displays similar characteristics in its ^1H 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.

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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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