The synthesis of Mo(IV) arene complexes by the hydrogenation of Mo(IV) olefin complexes†

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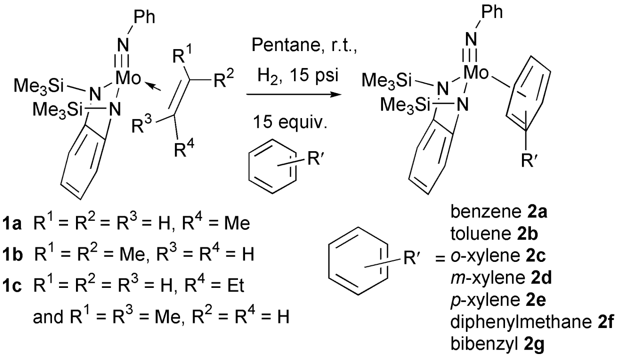
The compounds $[Mo(NPh)(\eta^2\text{-olefin})(o\text{-}(Me_3SiN)_2C_6H_4)]$ (olefin = propene (1a), isobutene (1b), and butenes (1c)) react with molecular hydrogen (*ca.* 15 psi) in the presence of excess arene affording Mo(IV) η^6-arene complexes of the type $[Mo(NPh)(\eta^6\text{-arene})(o\text{-}(Me_3SiN)_2C_6H_4)]$ (arene = benzene (2a), toluene (2b), *o*-xylene (2c), *m*-xylene (2d), *p*-xylene (2e), diphenylmethane (2f), and bibenzyl (2g)), while treatment of $[Mo(NPh)(\eta^2\text{-styrene})(o\text{-}(Me_3SiN)_2C_6H_4)]$ (1d) with hydrogen in a pentane solution gives $[Mo(NPh)(\eta^6\text{-ethylbenzene})(o\text{-}(Me_3SiN)_2C_6H_4)]$ (2h); the crystal structures of 2d and 2e are reported and reveal highly distorted arene ligands approaching η^4-coordination modes.

Fisher and Hafner characterized the first transition metal π-arene complex, $Cr(\eta^6\text{-benzene})_2$, 45 years ago.[1] Since this discovery the chemistry of π-arene complexes has been extensively explored.[2] It was initially believed that arene complexes were confined to transition metals in low oxidation states and a significant development in this field has involved the synthesis and characterization of high oxidation state Group 4 and 5 transition metal–arene complexes.[3,4] While Group 4 and 5 arene complexes are relatively rare, high valent Group 6 arene complexes are, with one exception,[5] non-existent. Furthermore, the generation of isolable high oxidation state transition metal–arene complexes *via* hydrogenation of η^2-olefin complexes remains a rare process.[6] We report herein the synthesis and structure of molybdenum(IV) η^6-arene complexes obtained upon exposure of various molybdenum η^2-olefin complexes,[7] of the form $[Mo(NPh)(\eta^2\text{-olefin})(o\text{-}(Me_3SiN)_2C_6H_4)]$, to molecular hydrogen (*ca.* 15 psi) and excess arene. In addition, these molybdenum(IV) η^6-arene complexes catalyse the hydrogenation of olefins.



Scheme 1

The hydrogenation of **1a**–**c** in the presence of 15 equivalents of arene gave complexes **2a**–**g** as microcrystals after crystallization from pentane (Scheme 1).§ The molecular structures of **2d** and **2e** were determined by single crystal X-ray diffraction studies, and are shown in Fig. 1 and 2, respectively, along with selected crystal data.¶ Complex **2d** adopts a three-legged piano stool geometry in which the arene ligand is strongly distorted toward an η^4-coordination mode. The structural data suggest that the interaction of the arene ligand with the molybdenum metal center is much like a 1,3-butadiene–metal interaction. A considerable ring distortion of 17.4(3)° was found between the planes formed by C(20)–C(19)–C(24)–C(23) and C(20)–C(21)–C(22)–C(23). Carbons C(19) and C(24) were found to be considerably further from the metal center than the other arene carbons, suggesting that the arene interaction with the metal center is mostly through C(20), C(21), C(22) and C(23). The shorter bond lengths for C(21)–C(22) and C(19)–C(24), in comparison with the remainder of the arene carbon–carbon bonds, are consistent with considerable double bond character between these carbons.

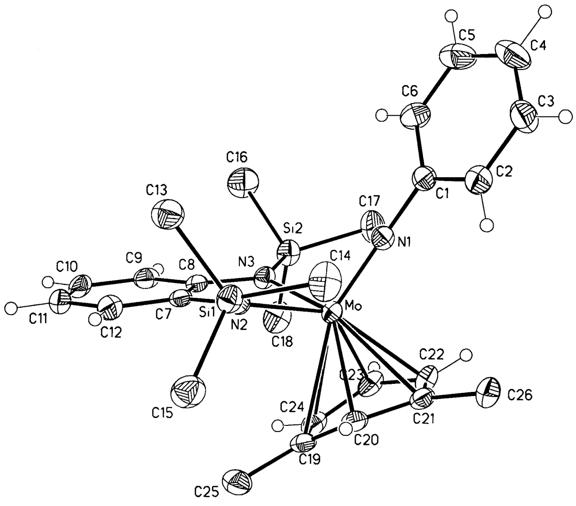


Fig. 1 Thermal ellipsoid plot of **2d** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Mo–N(1) 1.761(3), Mo–C(19) 2.519(3), Mo–C(20) 2.313(4), Mo–C(21) 2.425(4), Mo–C(22) 2.371(4), Mo–C(23) 2.286(4), Mo–C(24) 2.506(4), C(19)-C(20) 1.444(5), C(20)–C(21) 1.420(5), C(21)–C(22) 1.387(6), C(22)–C(23) 1.421(5), C(23)–C(24) 1.441(5), C(24)–C(19) 1.381(5); Mo–N(1)–C(1) 178.9(3).

Similar structural parameters were found for **2e** which has a ring distortion of 17.1(1)°. The Mo–N(1) bond lengths in both complexes are virtually identical at 1.761(3) (**2d**) and 1.775(1) Å (**2e**) and are consistent with a Mo–N triple bond interaction.[8] An interesting difference between the two structures arises upon comparison of the Mo–N(1)–C(1) angles which are 178.9(3) (**2d**) and 145.5(1)° (**2e**). It is tempting to suggest that this difference arises from a significant difference in the Mo–N(1) interaction between the two compounds. However, close inspection of the packing diagram of **2d** reveals that there is a π-stacking interaction between the phenyl rings of the phenyl imido groups of neighboring molecules. Given that calculations suggest a very soft bending potential for aryl imido complexes,[9] the differences in the Mo–N(1)–C(1) angles in **2d** and **2e** are most likely due to crystal packing forces.

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† Electronic supplementary information (ESI) available: ¹H NMR spectra for complexes **2b**–**2d** and **2h**, chemical shift data for **2a**–**2h**. See http://www.rsc.org/suppdata/cc/b0/b007812n/

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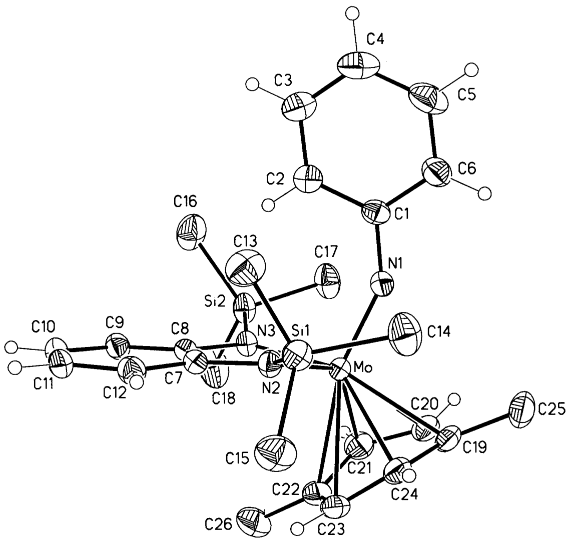
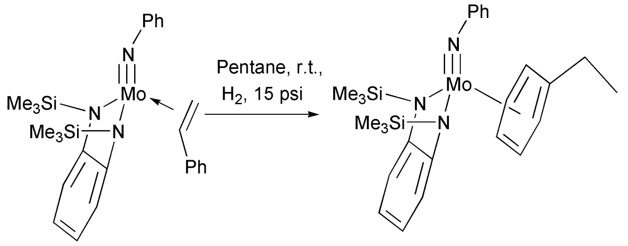


Fig. 2 Thermal ellipsoid plot of **2e** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Mo–N(1) 1.7746(14), Mo–C(19) 2.3908(17), Mo–C(20) 2.3900(18), Mo–C(21) 2.3243(19), Mo–C(22) 2.5637(19), Mo–C(23) 2.5410(18), Mo–C(24) 2.2981(18), C(19)–C(20) 1.392(3), C(20)–C(21) 1.4091(3), C(21)–C(22) 1.453(3), C(22)–C(23) 1.359(3), C(23)-C(24) 1.443(3), C(24)-C(19) 1.428(3), Mo-N(1)-C(1) 145.47(12).



Scheme 2

The chemical shifts associated with the arene protons in the ^{1}H NMR spectra of these complexes are shifted significantly upfield, appearing in the region spanning δ 4.5–5.5 as expected for η^6-bound arene ligands.[10] The arene resonances are well resolved in the ^{1}H NMR spectra at room temperature and only one resonance for the Me_3Si groups is observed, supporting a low barrier to arene ring rotation (ESI†).

When a pentane solution of **1d** was exposed to a slight pressure of dihydrogen (*ca.* 15 psi) for 15 min, **2h** formed and was isolated as a microcrystalline solid by crystallization and filtration at −78 °C (Scheme 2).§ The ^{1}H NMR spectrum of **2h** is similar to those of complexes **2a**–**g** (ESI†).

Compounds **2a**–**h** are catalysts for the hydrogenation of olefins. When C_6D_6 solutions of **2h** (1 mol%) and a substrate olefin (styrene, neohexene, or *trans*-stilbene) were exposed to low pressures of dihydrogen (*ca.* 15 psi) at room temperature, slow conversion to the respective alkanes was observed. Raising the temperature of the reaction to 50 °C increased the rate of hydrogenation of neohexene [1 mol%, (**2b**)] from 17% conversion overnight to 62% over 8 h (TOF *ca.* 7/h).

η^2-Olefin complexes have been widely proposed as intermediates in the catalytic hydrogenation of olefins. As the ethylbenzene ligand of **2h** is readily displaced by styrene giving **1d** at room temperature it is likely that the propagating species in the above hydrogenation reaction is indeed an olefin complex. In general, the arene ligands also undergo exchange reactions with C_6D_6 at room temperature with the rates of reaction depending to some extent upon the identity of the arene ligand that is being displaced.

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Notes and references

§ All reactions and manipulations were carried out using standard Schlenk techniques or in a dry box under a nitrogen atmosphere. Complexes **1a**–**d** were synthesized according to published procedures.[7] Synthesis of **2a**–**g**: to a pentane solution of freshly generated **1a**–**c**, 15 equivalents (relative to the Mo starting material) of the appropriate arene were added followed by freezing of the mixture and evacuation of the headspace. Dry hydrogen was then added to the thawed solution, which was stirred at room temperature for 30 min. The volatiles were then removed *in vacuo* affording **2a**–**g** as blue–green solids that were recrystallized from pentane at −78 °C (80–85% isolated yield). The synthesis of **2h** is analogous to **2a**–**g**; however, no excess arene is employed.

¶ *Crystal data*: for **2d**: $C_{26}H_{37}MoN_3Si_2$, M = 543.71, triclinic, space group $P\bar{1}$, a = 9.2793(6), b = 10.5045(7), c = 15.466(1) Å, α = 87.784(1), β = 76.796(1), γ = 64.068(1)°, V = 1316.7(2) Å^3, Z = 2, μ(Mo-Kα) = 0.608 mm^{-1}, T = 173(2) K, final $R1$ = 0.0453, $wR2$ = 0.0775, Gof (on F^2) = 1.021.

For **2e**: $C_{26}H_{37}MoN_3Si_2$, M = 543.71, monoclinic, space group $P2_1/n$, a = 9.7367(4), b = 14.3272(6), c = 19.5480(8) Å, α = 90, β = 95.080(1), γ = 90°, V = 2716.2(2) Å^3, Z = 4, μ(Mo-Kα) = 0.589 mm^{-1}, T = 173(2) K, final $R1$ = 0.0237, $wR2$ = 0.0590, Gof (on F^2) = 1.021.

CCDC 182/1881. See http://www.rsc.org/suppdata/cc/b0/b007812n/ for crystallographic files in .cif format.

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.[11] All non-hydrogen atoms included in calculated positions.

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