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Synthesis and Characterization of New d^0 Tungsten and Molybdenum Imido Complexes with Heteroatomic Bifunctional O–N Chelate Ligands

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New tungsten d^0 bis(imido) compounds of formula $W(NCMe_3)_2(O–N)_2$ (**2a–e**) (HO–N = 2-hydroxypyridine, 2-pyridinecarboxylic acid, 8-hydroxyquinoline, 8-hydroxyquinaldine, 2-(2-hydroxyphenyl)benzothiazole, and 2-(2-hydroxyphenyl)benzoxazole) have been prepared from the bis(amido) bis(imido) compound $W(NCMe_3)_2(NHCMe_3)_2$ (**1**) by protonation and subsequent replacement of the amido groups with heteroatomic chelate ligands of the type HO–N which are weak acids and strong nitrogen bases. Solution spectroscopic data suggest that the new hexacoordinate tungsten(VI) imido complexes are monomeric and six-coordinate with equivalent imido ligands. The four-coordinate molybdenum bis(imido) complex $Mo(NCMe_3)_2(OSiMe_3)_2$ (**3**) reacts with 1,2-dihydroxybenzene ($CatH_2$) in the presence of pyridine, yielding the six-coordinate compound of formula $Mo(NCMe_3)(Cat)(OSiMe_3)_2(Py)$ (**4**), while the reaction with 2 equiv of the heteroatomic chelate ligand 8-hydroxyquinoline yields the six-coordinate mixed oxo imido compound of formula $Mo(NCMe_3)(O)(N–O)_2$ (**5**) (HO–N = 8-hydroxyquinoline) by elimination of *tert*-butylamine and hexamethyldisiloxane. In a different manner, the protonation of the isoelectronic organomolybdenum species $Mo(NCMe_3)_2(Mes)_2$ (**6**) (Mes = 2,4,6-trimethylphenyl) with 1 equiv of 8-hydroxyquinoline or 8-hydroxyquinaldine results in the cleavage of one mesityl group, leading to the formation of five-coordinate compounds of formula $Mo(NCMe_3)_2(Mes)(O–N)$ (**7a,b**).

Introduction

Imido ligands are often used to stabilize high oxidation states of metals,[1] and many of the resultant complexes have found applications in catalysis.[2] The four-coordinate tungsten(VI) (d^0) bis(imido) bis(amido) compound $W(NCMe_3)_2(NHCMe_3)_2$,[3] which can be regarded formally as a 16-electron species (counting the imido ligands as six-electron-donating dianions and the amido ligands as two-electron-donating monoanions), was first reported by Nugent et al. in 1980.[3] Protonation of the amido functions with bulky alcohols such as *tert*-butyl alcohol and triphenylsilanol and the subsequent elimination of *tert*-butylamine allow the preparation of the corresponding coordinatively unsaturated alkoxy and siloxy species $W(NCMe_3)_2(OCMe_3)_2$ and $W(NCMe_3)_2(OSiPh_3)_2$, respectively.[3] Sterically less demanding strong Bronsted acids, such as HCl, HBF_4 etc., give neutral six-coordinate compounds with coordinating *tert*-$BuNH_2$ ligands.[4] In a continuation of our study of the application of heteroatomic chelate ligands to highly oxidized transition metals, we attempted to synthesize electronically and coordinatively saturated d^0 tungsten and molybdenum imido complexes. Our goal was the preparation of saturated six-coordinate bis(imido) complexes, in which mixed bonding environments for the imido ligands[1,5,6] were possible. So far, only one crystallographically characterized six-coordinate d^0 bis(imido) complex, $Mo(NPh)_2(S_2CNEt_2)_2$,[5] has shown (at −130 °C) both a linear and a strongly bent imido ligand with therefore definitively distinct bond orders of 3 and 2, respectively. All of the other known structures of bis(imido) complexes, $Cl_2W(NPh)_2(bipy)$,[6] $Cl_2(bipy)W(NPh)(NBu^t)$,[7] and the ionic complex[8] $[MeReCl_3(NC_6H_3Me_2\text{-}2,6)_2]^-$, show virtually identical metal–N(imido) bond lengths and very similar, slightly bent (170°) metal–N–C angles. The structure of $Mo(NBu^t)_2[\eta^2(N,O)\text{-}Bu^tNC(O)N(H)Bu^t][Bu^t(H)NC(O)]_2$, which has chemically different metal–imido units, shows similar metal–nitrogen distances but different angles.[9] This complex is not strictly comparable to the representative chelated complexes listed above, and it is difficult to make comparisons in this last case. All of these latter structures were determined at room temperature. The structure and reactivity of these imido species are of interest because a nitrogen atom in a bent imido group is expected to show greater nucleophilic character and therefore enhanced reactivity toward electrophiles compared to a linear imido substituent.

Results and Discussions

(a) Synthesis of New Bis(imido) d^0 Tungsten Complexes. In order to accomplish electronic saturation of the metal in tungsten bis(imido) complexes, the use of aromatic HO–N chelate ligands seemed promising, since these bifunctional compounds have a relatively strong protic function which can be used to protonate the amido groups in $W(NCMe_3)_2(NHCMe_3)_2$ as well as providing a hard base nitrogen donor. This latter feature is often an essential stabilizing component in high-oxidation-state metal complexes where the metal atom behaves as a hard Lewis acid. Indeed, the reaction of $W(NCMe_3)_2(NHCMe_3)_2$ with the heteroatomic chelate ligands 2-hydroxypyridine, 2-pyridinecarboxylic acid, 8-hydroxyquinoline, 8-hydroxyquinaldine, 2-(2-hydroxyphenyl)-benzothiazole, and 2-(2-hydroxyphenyl)benzoxazole proceeded smoothly according to Scheme 1, to produce the hexacoordinate four-, five-, and six-membered metallacyclic d^0 tungsten bis(imido) compounds in high yields as yellow microcrystalline solids.

The new species are soluble in common aprotic organic solvents and show only one type of *tert*-butyl signal in their ^1H NMR

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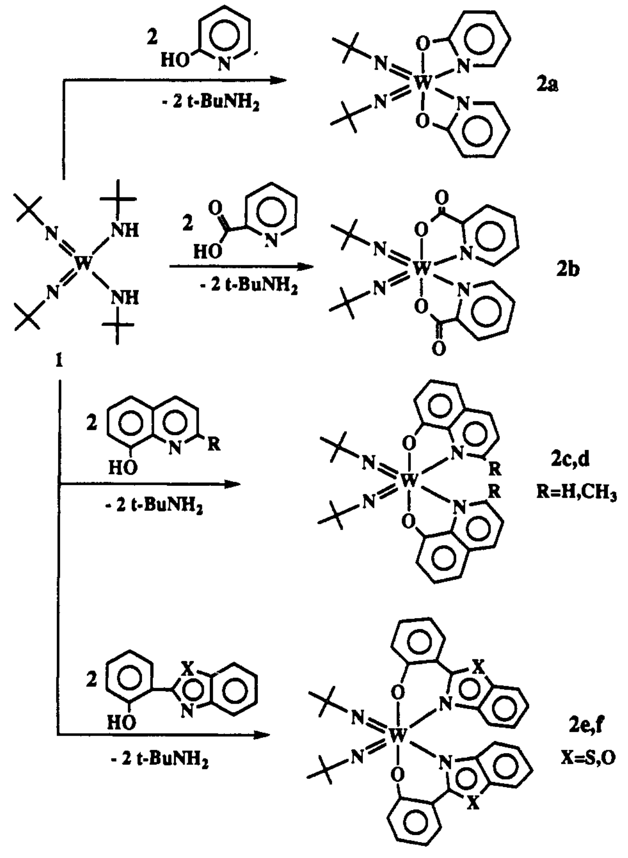
Table 1. ^{13}C Chemical Shift Data (ppm) for Selected Compounds

complex	quaternary C	methyl C (^tBu)	diff
2a	66.9	32.6	34.3
2b	67.1	31.7	35.4
2c	66.2	32.1	34.1
2d	66.3	32.1	34.2
2f	66.5	32.1	34.4
5	69.6	30.6	39.0
7a	69.2	31.3	37.9

Scheme 1



spectra as well as a simple pattern in the aromatic region, indicating a relatively symmetric structure with equivalent O–N chelate ligands. Considering the strong π-donor properties of the imido ligands and the weaker π-donor properties of the phenolato and carboxylato oxygen atoms, an octahedral structure with axial oxygen atoms and equatorial *cis* imido groups is proposed for **2a–e**. The nitrogen atom of the chelate ligands then occupies the remaining equatorial positions as depicted in Scheme 1. The sharing of π-bonding between the imido ligands (e.g. averaging) implies an average metal–nitrogen bond order between 2 and 3. The combination of the position of the ^{13}C chemical shift for the central carbon atom of the *tert*-butyl group and the difference between the chemical shift of the central and methyl carbon atoms has been suggested as a probe of the electronic structure of the *tert*-butylimido ligand.[10] Indeed, the ^{13}C spectra of selected compounds (Table 1) show that the central carbon atom of the *tert*-butyl group resonates at higher field than usually found for this type of ligand,[1,10,11] implying the expected electronic saturation in the complexes and the decreased metal–nitrogen bond order.

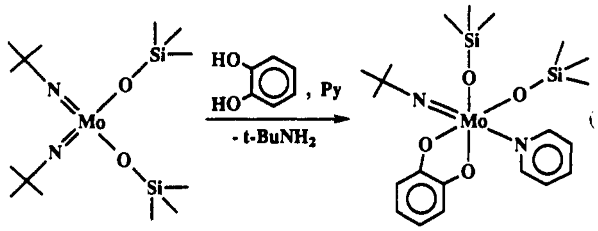
Unfortunately we have not been able so far to obtain X-ray-quality crystals for a detailed solid-state structural study of these compounds.

The IR spectra of these new compounds show a medium to strong absorption in the range 1290–1250 cm^{-1} which can be attributed to the metal–nitrogen multiple bond, although the assignment of metal–imido vibrations is often ambiguous.[1]

The reaction of **1** with HO–NH_2 type ligands such as 2-hydroxyaniline, anthranilic acid, etc. resulted in the formation of untractable mixtures. On the basis of their ^1H NMR spectra, it appears however that the NH_2 function of the chelate ligand is sufficiently acidic to protonate the remaining imido groups, leading to complex products.

Preliminary results indicate that some of the new complexes can serve as starting materials for the synthesis of bis(imido)-bis(aryl (alkyl))tungsten compounds.

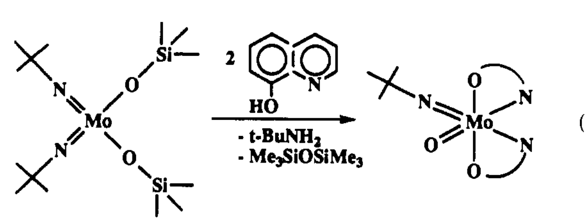
(b) Substitution Reactions of $Mo(NCMe_3)_2(OSiMe_3)_2$ (3) with Catechol and 8-Hydroxyquinoline. In spite the fact that the bis(imido)molybdenum compound $Mo(NCMe_3)_2(OSiMe_3)_2$ (**3**)[1] is formally a 16-electron complex (assuming that the imido and siloxy ligands act as six- and two-electron-donating anions, respectively), which implies a decreased nucleophilicity on the nitrogen atom, the reaction of this species with weak acids involves the protonation and substitution of the imido ligands. Thus, the reaction of **3** with a stoichiometric amount of 1,2-dihydroxybenzene (catechol) yielded a dark solution from which no pure compound could be isolated in the solid state. Further addition of 1 equivalent of pyridine yielded the dark greenish species of formula $Mo(NCMe_3)(1,2\text{-}O_2C_6H_4)(OSiMe_3)_2(Py)$ (**4**) according to eq 1. Interestingly, the mass spectrum of the compound shows, in addition to the peak at *m/e* 455 ($[M - Py]^+$), a group of peaks at *m/e* 748 with an isotope pattern typical of a bimetallic molybdenum species. This result is interpreted as the formation of an oxo-bridged molybdenum dimer of formula $[Mo(NCMe_3)(1,2\text{-}O_2C_6H_4)(OSiMe_3)]_2O$ by elimination of hexamethydisiloxane and pyridine from **4** under the conditions present in the spectrometer. Our attempts to synthesize this dimer by a controlled pyrolysis of **4** however failed to yield the desired product.



(1)

4

The reaction of $Mo(NCMe_3)_2(OSiMe_3)_2$ (**3**) with 1 equiv of 8-hydroxyquinoline yielded no characterizable compound, whereas employing 2 equiv of the ligand in refluxing hexane gave the mixed imido oxo complex of formula $Mo(NCMe_3)(O)(O\text{–}N)_2$ (**5**) according to eq 2. The replacement of one imido group by two chelating 8-oxyquinolinato ligands occupying four coordination sites probably leads to an overcrowded intermediate and subsequently to **5**. Although the mechanism of this reaction is unclear, it could be described overall as a heteroatomic chelate ligand induced formation of a terminal molybdenum–oxo multiple bond by elimination of hexamethyldisiloxane. The IR spectrum shows a strong band at 886 cm^{-1} which is assigned to the terminal



(2)

5

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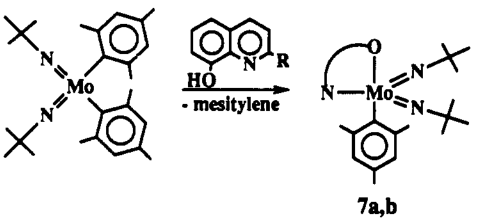
molybdenum–oxo vibration. In the ^{1}H NMR spectrum of **5** the aromatic region indicates two types of oxine ligand. This observation, together with the fact that strong π-donor ligands such as the oxo and imido groups in **5** prefer a mutual *cis* arrangements which reduces mutual competition,[1] leads us to propose the structure depicted in eq 2. It is of interest to note that the structurally characterized analogous dioxo compound $MoO_2(C_9H_6NO)_2$ has equatorial *cis* oxo ligands, while the axial as well as the remaining equatorial positions of the octahedra are occupied by the oxygen and nitrogen atoms of the 8-oxyquinolinato ligands, respectively, in a manner similar to the structure proposed for **5**.[12]

(c) Substitution Reactions of $Mo(NCMe_3)_2(Mes)_2$ (6) with 8-Hydroxyquinoline and 8-Hydroxyquinaldine. The four-coordinate organomolybdenum species $Mo(NCMe_3)_2(Mes)_2$ (**6**)[13] is isoelectronic with **3**. The reactions of this bis(imido) complex with 1 equiv of the heteroatomic chelate ligands 8-hydroxyquinoline and 8-hydroxyquinaldine result in the substitution of one mesityl group and yield the five-coordinate compounds of formula $Mo(NCMe_3)_2(Mes)(O\text{–}N)$ (**7a,b**) and mesitylene. Although the initial protonation of the imido nitrogen atom and subsequent hydrogen transfer to the mesityl group cannot be excluded, these reactions reflect the relatively labile character of the Mo–C bond in **6** toward protic attack as compared with the chromium analogue $Cr(NCMe_3)_2(Mes)_2$.[11] Related high-oxidation-state group VII and VIII organometallic oxo species, for example $ReO_2(Mes)_2$, $ReO(Mes)_4$, and $OsO_2(Mes)_2$,[14] are hydrolytically stable. The ^{1}H NMR spectra of **7a,b** show only one type of imido ligand. On the basis of this information, we propose a trigonal bipyramidal structure with *cis* imido groups as depicted in eq 3. The broad ortho methyl signals in the spectrum of **7b** also indicate a restricted rotation of the mesityl ligand.[14,15]



(3)

7a,b
R = H, CH$_3$

Conclusion

Saturated six-coordinate d^0 bis(imido) complexes of tungsten are readily available from the protonation and amine elimination of bis(amido)bis(imido)tungsten compounds with bifunctional hydroxy ligands. These complexes are monomeric, showing equivalent imido ligands in solution. Isoelectronic Mo complexes under similar conditions suffered cleavage of one mesityl group with formation of five-coordinate compounds; thus the Mo chemistry is not parallel to that of tungsten.

Experimental Section

All reactions were carried out under an argon atmosphere using conventional Schlenk apparatus. Complexes **1** and **3** were prepared as described previously.[3] Solvents were dried and stored under argon. The ^{1}H NMR spectra were recorded on a 200-MHz Bruker spectrometer, while the mass spectra were recorded on an AE MS12 spectrometer. The *m/e* values are based on the ^{184}W and ^{98}Mo isotopes.

(i) Synthesis of Bis(*tert*-butylimido)bis(2-pyridinolato)tungsten (2a). A 190-mg sample (2.0 mmol) of 2-hydroxypyridine dissolved in 4 mL of toluene was added dropwise to a hexane solution (15 mL) of 470 mg (1.0 mmol) of **1**. The pale yellow solution was refluxed for 5 min and then stirred at room temperature for 1 h. The solvent was stripped off in vacuo, and the residue was extracted with hexane. After filtration of the extract, the solvent was removed in vacuo, yielding a sticky amorphous solid (**2a**). Yield: 318 mg, 62%. Mp: 85 °C. Anal. Found (calcd) for $C_{18}H_{26}N_4O_2W$: C, 41.62 (42.03); H, 5.11 (5.10); N, 10.28 (10.89). IR (KBr; cm^{-1}): 2977 m, 1654 s, 1604 s, 1541 m, 1425 m, 857 m, 778 s. ^{1}H NMR (25 °C, CD_2Cl_2): δ 1.35 (s, 18H, NC_4H_9), 6.49 (m, 2H, 3-H of NC_5H_4O), 6.61 (m, 2H, 4-H of NC_5H_4O), 7.50 (m, 2H, 5-H of NC_5H_4O), 7.72 (m, 2H, 6-H of NC_5H_4O). MS *m/e* (relative intensity, %): 514 ($[M]^+$, 8), 499 ($[M - CH_3]^+$, 100), 443 ($[M - CH_3 - C_4H_8]^+$, 20).

(ii) Synthesis of Bis(*tert*-butylimido)bis(2-pyridinecarboxylato)tungsten–0.5-Toluene (2b). A toluene solution (15 mL) of 470 mg (1.0 mmol) of **1** and 246 mg (2.0 mmol) of picolinic acid was stirred at 40 °C for 15 min and then at room temperature for 1 h. Reducing the volume of the solution in vacuo and cooling to –20 °C yielded yellow crystals of **2b**, which were separated from the mixture by decanting the mother liquor. Further concentration of the mother liquor and addition of *n*-hexane gave an additional crop of **2b**. Combined yield: 560 mg, 91%. Mp: 146 °C. Anal. Found (calcd) for $C_{20}H_{26}N_4O_4W{\cdot}0.5tol$: C, 45.98 (45.79); H, 4.97 (4.91); N, 8.78 (9.09). IR (KBr; cm^{-1}): 2960 m, 1690 vs, 1605 m, 1325 m, 1282 s, 1258 s, 1145 s, 1041 m, 1019 m, 862 s, 770 m, 693 m, 638 m, 452 m. ^{1}H NMR (25 °C, CD_2Cl_2): δ 1.16 (s, 18H, NC_4H_9), 7.6 (m, 2H, 5-H of $C_6H_4NO_2$), 8.0 (m, 2H, 4-H of $C_6H_4NO_2$), 8.15 (m, 2H, 3-H of $C_6H_4NO_2$), 9.7 (m, 2H, 6-H of $C_6H_4NO_2$). MS *m/e* (relative intensity, %): 570 ($[M]^+$, 10), 555 ($[M - CH_3]^+$, 100), 514 ($[M - C_4H_8]^+$, 35).

(iii) Synthesis of Bis(*tert*-butylimido)bis(8-oxyquinolinato)tungsten(VI) (2c) and Bis(*tert*-butylimido)bis(8-oxyquinaldinato)tungsten(VI) (2d). To a hexane solution (15 mL) of **1** (728 mg, 1.55 mmol) was added 3.0 mmol of 8-hydroxyquinoline or 8-hydroxyquinaldine, and the mixture was refluxed for 2 min. As the yellow solution was cooled to room temperature, part of the product precipitated. Stirring was continued for 30 min; then the mixture was concentrated in vacuo and cooled to –30 °C, and the product was filtered off. Washing with a small amount of cold *n*-hexane and drying in vacuo afforded analytically pure compounds.

2c. Yield: 801 mg, 87%. Mp: 221 °C. Anal. Found (calcd) for $C_{26}H_{30}N_4O_2W$: C, 50.37 (50.82); H, 5.00 (4.92); N, 8.94 (9.11). IR (KBr; cm^{-1}): 2966 m, 1574 s, 1498 s, 1468 s, 1374 s, 1321 s, 1278 s, 1250 s, 1107 s, 823 s, 749 s, 741 s. ^{1}H NMR (25 °C, CD_2Cl_2): δ 1.09 (s, 18H, NC_4H_9), 7.1–8.5 (m, 12H, C_9H_6NO). MS *m/e* (relative intensity, %): 614 ($[M]^+$, 100), 599 ($[M - CH_3]^+$, 74), 543 ($[M - NC_4H_9]^+$, 5), 486 ($[M - NC_4H_9 - C_4H_9]^+$, 20).

2d. Yield: 808 mg, 84%. Mp: 162 °C. Anal. Found (calcd) for $C_{28}H_{34}N_4O_2W$: C, 51.70 (52.34); H, 5.36 (5.33); N, 8.55 (8.72). IR (KBr; cm^{-1}): 2966 m, 1566 m, 1505 m, 1467 m, 1430 s, 1328 s, 1277 vs, 1107 s, 830 m, 754 s. ^{1}H NMR (25 °C, CD_2Cl_2): δ 1.22 (s, 18H, NC_4H_9), 2.84 (s, 6H, $C_9H_5ONCH_3$), 7.05–7.98 (m, 10H, $C_9H_5NOCH_3$). MS *m/e* (relative intensity, %): 642 ($[M]^+$, 20), 627 ($[M - CH_3]^+$, 100), 612 ($[M - CH_3 - CH_3]^+$, 8), 571 ($[M - NC_4H_9]^+$, 10), 514 ($[M - NC_4H_9 - C_4H_9]^+$, 20).

(iv) Synthesis of Bis(*tert*-butylimido)bis(2-benzothiazolyl-2-phenolato)tungsten (2e) and Bis(*tert*-butylimido)bis(2-benzoxazolyl-2-phenolato)tungsten (2f). To a toluene solution (12 mL) of **1** (493 mg, 1.05 mmol) was added 2.0 mmol of the chelate ligand. The yellow solution was refluxed for 2 min; then it was cooled to room temperature and concentrated in vacuo to ca. 2 mL. Addition of hexane (10 mL) and cooling to –20 °C gave **2e** and **2f** as yellow microcrystalline solids, which were filtered off, washed with *n*-hexane, and dried in vacuo.

2e. Yield: 746 mg, 96%. Mp: 238 °C. Anal. Found (calcd) for $C_{34}H_{34}N_4O_2S_2W$: C, 51.98 (52.44); H, 4.45 (4.40); N, 6.92 (7.19). IR (KBr; cm^{-1}): 2970 w, 2920 w, 1600 m, 1488 s, 1479 s, 1449 s, 1237 s, 880 m, 768 s, 761 s, 754 s, 618 m. ^{1}H NMR (25 °C, CD_2Cl_2): δ 0.95 (s, 18H, NC_4H_9), 6.9–7.9 (m, 16H, $C_{13}H_8NOS$). MS *m/e* (relative intensity, %): 778 ($[M]^+$, 1), 763 ($[M - CH_3]^+$, 22), 707 ($[M - NC_4H_9]^+$, 5), 650 ($[M - NC_4H_9 - C_4H_9]^+$, 12).

2f. Yield: 723 mg, 97%. Mp: 258 °C. Anal. Found (calcd) for $C_{34}H_{34}N_4O_4W$: C, 55.20 (54.70); H, 4.63 (4.59); N, 7.39 (7.50). IR (KBr; cm^{-1}): 2966 w, 2915 w, 1609 s, 1541 m, 1471 s, 1454 m, 1304 m, 1255 s, 1241 s, 1057 m, 863 m, 803 m, 759 s, 738 s, 615 m. ^{1}H NMR (25 °C, CD_2Cl_2): δ 0.98 (s, 18H, NC_4H_9), 6.90–8.16 (m, 16H, $C_{13}H_8NO_2$). MS *m/e* (relative intensity, %): 746 ($[M]^+$, 4), 731 ($[M - CH_3]^+$, 100), 675 ($[M - NC_4H_9]^+$, 12).

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(v) Synthesis of (Pyridine)(*tert*-butylimido)(catecholato)bis(trimethylsiloxo)molybdenum (4). To a hexane solution (20 mL) of **3** (416 mg, 1.0 mmol) were added 88 μL (1.1 mmol) of pyridine and 110 mg (1.0 mmol) of catechol. The reaction mixture was stirred for 90 min; then the dark greenish solution was filtered. The filtrate was concentrated in vacuo, and upon cooling of the mixture to –78 °C, the product crystallized as a shining dark greenish microcrystalline solid. Recrystallization from *n*-hexane gave analytically pure **4**. Yield: 372 mg, 70%. Anal. Found (calcd) for $C_{21}H_{36}NO_4Mo$: C, 47.48 (47.35); H, 6.92 (6.81); N, 4.78 (5.26). ^1H NMR (25 °C, C_6D_6): δ 0.33 (s, 18H, $OSiC_3H_9$), 1.38 (s, 9H, NC_4H_9), 6.37–8.16 (m, 9H, aromatic H). MS *m/e* (relative intensity, %): 455 ([M – Py]+, 4), 399 ($[M - Py - C_4H_8]^+$, 4), 293 ($[M - Py - (Me_3Si)_2O]^+$, 18), 79 ($[Py]^+$, 100).

(vi) Synthesis of (*tert*-Butylimido)oxobis(8-oxyquinolinato)molybdenum (5). To an *n*-hexane solution (10 mL) of **3** (416 mg, 1.0 mmol) was added 8-hydroxyquinoline (290 mg, 2.0 mmol) and the solution was refluxed for 5 min. After cooling of the sample to room temperature, the solution was evaporated to dryness. The residue was taken up in a small amount of *n*-hexane, the mixture was filtered, and the filtrate was cooled to –78 °C. The product precipitated as a yellow solid and was separated from the mixture by decanting the orange mother liquor. Recrystallization from *n*-hexane afforded analytically pure **5**. Yield: 320 mg, 68%. Anal. Found (calcd) for $C_{22}H_{21}N_2O_3Mo$: C, 56.62 (56.06); H, 4.52 (4.49); N, 8.60 (8.91). IR (KBr; cm^{-1}): 2960 w, 1576 m, 1497 vs, 1467 s, 1374 s, 1322 s, 1247 s, 1105 s, 886 s, 825 m, 744 s. ^1H NMR (25 °C, CD_2Cl_2): δ 1.15 (s, 9H, NC_4H_9), 7.1–8.7 (m, 12H, C_9H_6NO). MS *m/e* (relative intensity, %): 473 ($[M]^+$, 40), 458 ($[M - CH_3]^+$, 8), 402 ($[M - NC_4H_9]^+$, 20), 346 ($[M - NC_4H_9 - C_4H_9]^+$, 100).

(vii) Synthesis of Bis(*tert*-butylimido)(2,4,6-trimethylphenyl)(8-oxyquinolinato)molybdenum (7a) and Bis(*tert*-butylimido)(2,4,6-trimethylphenyl)(8-oxyquinaldinato)molybdenum (7b). A 476-mg sample (1.0 mmol) of **6** and 145 mg (1.0 mmol) of 8-hydroxyquinoline were dissolved in 35 mL of hexane, and the mixture was stirred overnight. Then the yellow solution was filtered, and the filtrate was evaporated to dryness in vacuo, leaving **7a** as a sticky microcrystalline solid. The residual mesitylene was removed by washing the microcrystalline material with a small amount of cold hexane. **7b** was prepared in a similar manner.

7a. Yield: 456 mg, 91%. Mp: 156 °C. Anal. Found (calcd) for $C_{26}H_{35}N_{30}Mo$: C, 61.83 (62.26); H, 7.18 (7.03); N, 8.05 (8.38)%. IR (KBr; cm^{-1}): 2970 m, 2920 m, 1575 m, 1499 s, 1468 s, 1376 s, 1320 s, 1246 s, 1236 s, 1198 s, 1106 s, 826 s, 750 s. ^1H NMR (25 °C, CD_2Cl_2): δ 1.31 (s, 18H, NC_4H_9), 2.21 (s, 6H, mesityl 2,6-CH_3), 2.22 (s, 3H, mesityl 4-CH_3), 6.75 (s, 2H, mesityl 3,5-H), 7.05–8.21 (m, 6H, C_9H_6-ON). MS *m/e* (relative intensity, %): 504 ($[M]^+$, 18), 447 ($[M - C_4H_9]^+$, 21), 390 ($[M - C_4H_9 - C_4H_9]^+$, 14), 57 ($[C_4H_9]^+$, 100).

7b. Yield: 422 mg, 82%. Anal. Found (calcd) for $C_{27}H_{37}N_{30}Mo$: C, 63.14 (62.91); H, 7.39 (7.24); N, 7.53 (8.15). IR (KBr; cm^{-1}): 2968 s, 2919 s, 1564 m, 1505 m, 1461 s, 1430 s, 1325 m, 1274 m, 1250 s, 1202 s, 1111 m, 756 m, 630 m. ^1H NMR (25 °C, CD_2Cl_2): δ 1.36 (s, 18H, NC_4H_9), 2.04 (s, 6H, mesityl 2,6-CH_3), 2.18 (s, 3H, mesityl 4-CH_3), 2.31 (s, 3H, C_9H_5NO–CH_3), 7.02–8.11 (m, 5H, C_9H_5NO–CH_3). MS *m/e* (relative intensity, %): 517 ($[M]^+$, 100), 502 ($[M - CH_3]^+$, 5), 445 ($[M - CH_3 - C_4H_9]^+$, 40).

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