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Group 6 Imido Complexes Supported by Diamido-Donor Ligands

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Reactions of the lithiated diamido-pyridine or diamido-amine ligands $Li_2N_2N_{py}$ or $Li_2N_2N_{am}$ with $[W(NAr)Cl_4(THF)]$ (Ar = Ph or 2,6-$C_6H_3Me_2$; THF = tetrahydrofuran) afforded the corresponding imido-dichloride complexes $[W(NAr)(N_2N_{py})Cl_2]$ (R = Ph, **1**, or 2,6-$C_6H_3Me_2$, **2**) or $[W(NAr)(N_2N_{am})Cl_2]$ (R = Ph, **3**, or 2,6-$C_6H_3Me_2$, **4**), respectively, where N_2N_{py} = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ and N_2N_{am} = $Me_3SiN(CH_2CH_2NSiMe_3)_2$. Subsequent reactions of **1** with MeMgBr or PhMgCl afforded the dimethyl or diphenyl complexes $[W(NPh)(N_2N_{py})R_2]$ (R = Me, **5**, or Ph, **6**), respectively, which have both been characterized by single crystal X-ray diffraction. Reactions of $Li_2N_2N_{py}$ or $Li_2N_2N_{am}$ with $[Mo(NR)_2Cl_2(DME)]$ (R = ^tBu or Ph; DME = 1,2-dimethoxyethane) afforded the corresponding bis(imido) complexes $[Mo(NR)_2(N_2N_{py})]$ (R = ^tBu, **7**, or Ph, **8**) and $[Mo(N^tBu)_2(N_2N_{am})]$ (**9**).

Introduction

The use of chelating polyamide ligands to support organometallic and related compounds has received considerable attention in the past decade.[1] The use of bis(amido) compounds especially has been the subject of studies into "post-metallocene" olefin polymerization catalysts, and this area has been the subject of several recent reviews.[1,2] We have previously reported on the use of the chelating diamido-donor ligands $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ (N_2N_{py}) and $Me_3SiN(CH_2CH_2NSiMe_3)_2$ (N_2N_{am}) to support group 4 and group 5 imido chemistry.[3] We have also recently reported on the use of diamido-donor ligands in the organometallic chemistry of scandium.[4] In continuation of this work, we have been interested in extending the use of these chelating diamido-donor ligands to group 6 imido chemistry. In this regard, we were inspired in our efforts by the recent elegant studies by Boncella and co-workers of molybdenum and tungsten imido compounds containing chelating diamide ligands.[5] We have presented some preliminary results in a recent communication,[6] and we herein report the synthesis and characterization of a range of tungsten and molybdenum imido complexes supported by the N_2N_{py} and N_2N_{am} diamido-donor ligands.

Results and Discussion

Reactions of the lithiated amide $Li_2N_2N_{py}$ with the tungsten imido compounds $[W(NR)Cl_4(THF)]$ (R = Ph, 2,6-$C_6H_3Me_2$) are summarized in eq 1. The tungsten diamido-pyridine compounds $[W(NPh)(N_2N_{py})Cl_2]$ (**1**) and $[W(N\text{-}2,6\text{-}C_6H_3Me_2)(N_2N_{py})Cl_2]$ (**2**) were obtained as dark red-brown solids in 84% and 8% isolated yields, respectively, after workup. The low yield of **2** has been attributed to the high solubility in nonpolar organic solvents, making efficient crystallization problematic, since NMR tube scale experiments (C_6D_6) indicated virtually quantitative formation of **2** from $Li_2N_2N_{py}$ and $[W(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_4(THF)]$.

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(1) Gade, L. H. *Chem. Commun.* **2000**, 173 (feature article). Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468.

(2) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283.

(3) For a recent review of diamido-donor supported imido compounds see: Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216–217*, 65.

(4) Ward, B. D.; Maisse-François, A.; Dubberley, S. R.; Gade, L. H.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **2002**, 2649.

(5) For selected recent examples see: Cameron, T. M.; Gamble, A. S.; Abboud, K. A.; Boncella, J. M. *Chem. Commun.* **2002**, 1148. Mills, R. C.; Abboud, K. A.; Boncella, J. M. *Chem. Commun.* **2001**, 1506. Mills, R. C.; Wang, S. Y. S.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **2001**, *40*, 5077. Cameron, T. M.; Abboud, K. A.; Boncella, J. M. *Chem. Commun.* **2001**, 1224. Cameron, T. M.; Ortiz, C. G.; Ghiviriga, I.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2001**, *20*, 2032. Cameron, T. M.; Ghiviriga, I.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2001**, *20*, 4378.

(6) Ward, B. D.; Clot, E.; Dubberley, S. R.; Gade, L. H.; Mountford, P. *Chem. Commun.* **2002**, 2618.

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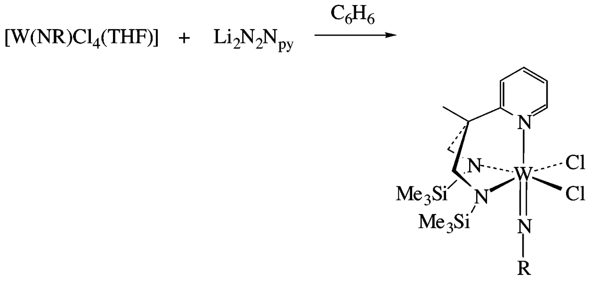


R = Ph (**1**) or 2,6-$C_6H_3Me_2$ (**2**)

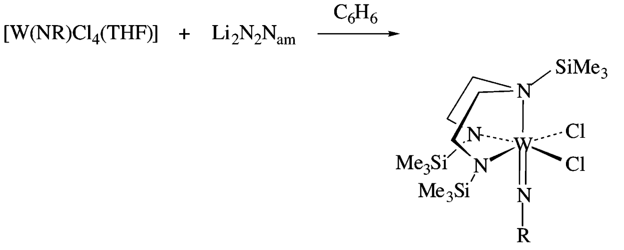
The NMR spectra of [W(NPh)(N_2N_{py})Cl_2] (**1**) display resonances attributable to a κ^3-coordinated N_2N_{py} ligand and the expected resonances attributed to the N-bound phenyl group. The distribution of the resonances support the C_s symmetric structure proposed in eq 1 (for example, there is a single signal of relative intensity 18 H observed for the two chemically equivalent $SiMe_3$ groups). The spectrum also shows a highly second order AB quartet around 3.82 ppm for the two sets of inequivalent N_2N_{py} methylene protons. We have previously demonstrated that the chemical shift of the pyridyl H^6 (i.e., bound to the carbon adjacent to N) resonance can be indicative of the coordinative state of the pyridyl group.[7] Thus, a downfield shift of the H^6 resonance relative to that in the $H_2N_2N_{py}$ protio ligand (e.g., $\delta = 8.47$ ppm in C_6D_6) indicates that the pyridyl "arm" is probably coordinated to the metal center. The H^6 proton resonance in the ^{1}H NMR spectrum of **1** is observed at 10.27 ppm, establishing that the pyridyl group is coordinated to tungsten, giving a *fac*-κ^3-coordinated N_2N_{py} ligand.

The NMR data for [W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] (**2**) are also consistent with a C_s symmetric structure. The only notable difference between the NMR spectra of **2** and those of **1** is the restricted rotation about the aryl ring-N bond on the NMR time scale. The aryl ring thus gives rise to two *ortho*-methyl signals in the ^{1}H and ^{13}C NMR spectra. A spin saturation transfer ^{1}H NMR experiment showed that the methyl groups are in slow exchange. However, the signals in the (300.2 MHz) ^{1}H NMR spectrum did not coalesce even at 110 °C, although significant broadening of the signals was observed at this temperature. The activation parameters for the rotation of the aryl group were obtained by line width analysis as discussed in following paragraphs.

Similarly, $Li_2N_2N_{am}$ reacts with [W(NR)Cl_4(THF)] (R = Ph, 2,6-$C_6H_3Me_2$) in benzene to afford [W(NPh)(N_2N_{am})Cl_2] (**3**) and [W(N-2,6-$C_6H_3Me_2$)(N_2N_{am})Cl_2] (**4**) as very soluble golden brown solids in 29% and 15% isolated yields, respectively (eq 2). The low isolated yields are attributed to the high solubilities, with NMR tube scale reactions in C_6D_6 proceeding in near-quantitative fashion. The NMR data for **3** and **4** support the proposed C_s symmetrical structures which are analogous to those for compounds **1** and **2** as described. The ^{1}H NMR spectra of both compounds feature two $SiMe_3$ resonances in a 9 H/18 H ratio, for the amine- and amide-nitrogen bound $SiMe_3$ groups, respectively. In each case, the N_2N_{am} methylene proton signals appear as four inequivalent multiplet resonances (relative intensity 2 H each) between 4.2 and 2.3 ppm. In contrast to the situation for **2**, the imido N-substituent in **4** does not show evidence for restricted rotation about the Ar−N bond on the NMR time scale, and no significant broadening of the *ortho*-methyl resonance was observed when the spectrum was recorded at −90 °C (500.0 MHz). The difference is attributed to the different chelate ring sizes for the N_2N_{py} (six-membered) and N_2N_{am} (five-membered) ligands and associated greater steric crowding in **2** compared to **4**.

Table 1. Corrected Linewidths ($\nu_{1/2}$(corr), Hz) and Observed Rate Constants (k_{obs}, s^{-1}) for *ortho*-Methyl Group Exchange in [W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] (**2**)

	$Me_A \rightarrow Me_B$		$Me_B \rightarrow Me_A$	
temp (K)	$\nu_{1/2}$(corr)	k_{obs}	$\nu_{1/2}$(corr)	k_{obs}
343	1.3	4.1	1.8	5.7
348	2.2	7.0	2.8	8.8
353	3.1	9.8	4.1	13
358	4.7	15	5.8	18
363	6.8	21	8.4	26
368	9.5	30	11.6	36.5
373	13.7	43.1	16.0	50.2
378	18.8	59.0	22.0	69.0



R = Ph (**3**) or 2,6-$C_6H_3Me_2$ (**4**)

Activation parameters for the exchange of the two methyl groups (arbitrarily denoted Me_A and Me_B) in [W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] (**2**, eq 3) were obtained by the line width analysis of eight measurements of the ^{1}H NMR spectrum (300.2 MHz) at temperatures between 343 and 378 K at intervals of 5 K in toluene-d_8. In each case, the line widths at half-height, $\nu_{1/2}$(obs), were corrected by subtracting the natural line widths obtained from the low temperature limit ^{1}H NMR spectrum recorded at 293 K. The values of $\nu_{1/2}$(corr) were used to calculate the observed rate constants (k_{obs}) for the processes $Me_A \rightarrow Me_B$ {k_{obs}(A → B)} and $Me_B \rightarrow Me_A$ {k_{obs}(B → A)} according to the formula $k_{obs} = \pi\nu_{1/2}$(corr).[8] The values of these rate constants are presented in Table 1 and have been used to construct Eyring plots (Figure 1) assuming that the chemical exchange rate constant k_c is equal to twice the observed rate constant k_{obs} since the conversion of environment A to B occurs at the same rate as the conversion from environment B to A.[9] The Eyring plot-derived values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and their corresponding values of $\Delta G^{\ddagger}_{298}$ (Gibbs free energy of activation at 298 K),

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(7) Friedrich, S.; Schubart, M.; Gade, L. H.; Scowen, I. J.; Edwards, A. J.; McPartlin, M. *Chem. Ber./Recl.* **1997**, *130*, 1751.

(8) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1992.

(9) Green, M. L. H.; Wong, L.-L.; Sella, A. *Organometallics* **1992**, *11*, 2660.

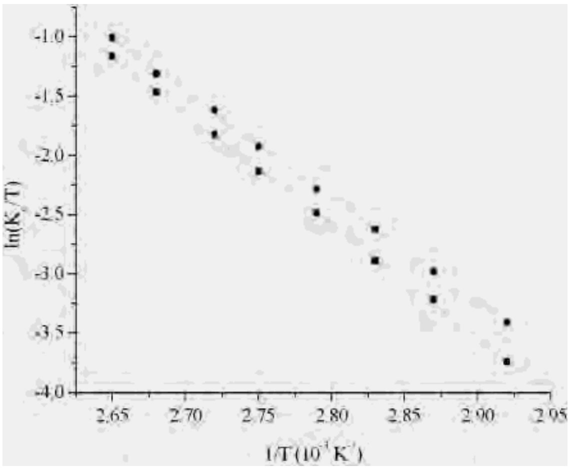
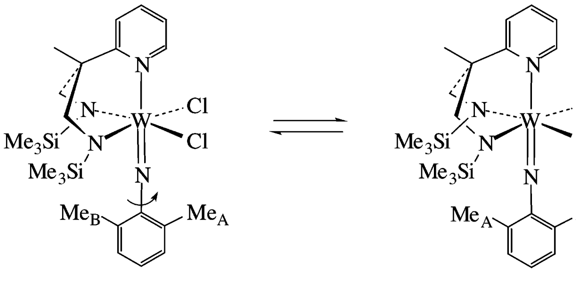


Figure 1. Eyring plots for *ortho*-methyl group exchange in [W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] (**2**). The individual lines correspond to independent measurements on the two methyl resonances, arbitrarily labeled "A" and "B" (upper line is for $Me_B \rightarrow Me_A$; lower is for $Me_A \rightarrow Me_B$).

Table 2. Activation Parameters for *ortho*-Methyl Group Exchange in [W(N-2,6-$C_6H_3Me_2$)(N_2N_{Py})Cl_2] (**3**)

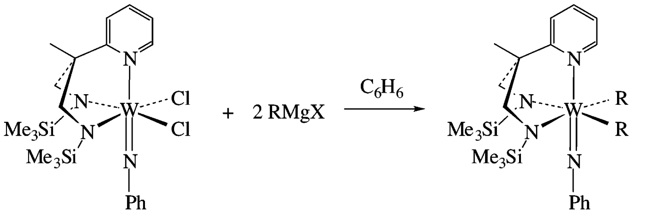
	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})
$Me_A \rightarrow Me_B$	77.9 ± 0.5	−1 ± 1	78.2 ± 0.8
$Me_B \rightarrow Me_A$	73.4 ± 0.5	−12 ± 1	77.0 ± 0.8
averaged values	75.6 ± 2.8	−6 ± 7	77.4 ± 4.9

were extracted (Table 2). The values obtained for the activation parameters are consistent with expected values for this system. The small (ca. zero) value for $\Delta S^{\ddagger}$ is indicative of a nondissociatively activated exchange process; in other words, the potentially labile[7] pyridyl moiety does not detach from the metal center during the process.



Following on from the synthesis of the tungsten dichloride compounds already discussed, it was of interest to prepare corresponding dialkyl and related compounds in order to probe the reactivity of such systems. Because [W(NPh)-(N_2N_{py})Cl_2] (**1**) was the only dichloride compound which could be prepared in synthetically useful quantities, further studies concentrated on this system alone.

Compound **1** reacts with 2 equiv of MeMgBr or PhMgCl in benzene to afford the dialkyl compounds [W(NPh)(N_2N_{py})-R_2] (R = Me, **5**, or Ph, **6**) (eq 4). Reaction with the corresponding organolithium reagents leads to decomposition. The dimethyl compound [W(NPh)(N_2N_{py})Me_2] (**5**) was obtained as a red solid in 35% isolated yield after workup, and the diphenyl compound [W(NPh)(N_2N_{py})Ph_2] (**6**) was obtained as a brown solid in 23% yield. The isotopically enriched compounds [W(NPh)(N_2N_{py})($^{13}CH_3$)$_2$], **5-^{13}C$_2$**, and [W(NPh)(N_2N_{py})(CD_3)$_2$], **5-*d*$_6$**, were prepared by methods analogous to those of compound **5** using $^{13}CH_3MgI$ and CD_3-MgI, respectively. The only notable difference in the preparative procedure was that it was important to add 1,4-dioxane (to precipitate magnesium salts) to the reaction mixture prior to workup in order to obtain the required product. Adding 1,4-dioxane to the preparation of **5** did not influence the outcome of the reaction.



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R = Me (**5**) or Ph (**6**)

All other attempted alkylation reactions of [W(NPh)-(N_2N_{py})Cl_2] (**1**) with alkyl lithium reagents RLi (R = Me or CH_2SiMe_3) or Grignard reagents RMgX (R = Et, CH_2Ph, CH_2SiMe_3, CH_2CMe_2Ph, or C_3H_5) were unsuccessful and gave complex mixtures from which no single product could be isolated. This contrasts with the work of Boncella, who has reported many different dialkyl derivatives of tungsten containing an imido and chelating bis(amido) co-ligands. This group also observed that the dialkyl derivatives were only accessible using Grignard reagents, and that reaction with lithium alkyls resulted in complex mixtures.[10] Additionally, Boncella has shown that the dialkyl compounds [W(NPh)-{(*o*-Me_3SiN)$_2C_6H_4$}R_2] (R = Et, ^{n}Pr or CH_2CH_2Ph) undergo β-hydrogen elimination in the presence of added base.[11] It is possible that the pyridyl donor of the N_2N_{py} ligand induces a similar behavior with dialkyls containing β-hydrogens, thus providing a decomposition pathway giving rise to ill-defined products for dialkyls other than those which contain no β-hydrogens.

The X-ray crystal structure of [W(NPh)(N_2N_{py})Me_2] (**5**) has been determined and supports that proposed in eq 4. The molecular structure of **5** is shown in Figure 2, and selected bond lengths and angles are presented in Table 3. Molecules of **5** possess a distorted octahedral geometry at tungsten. The imido ligand lies *trans* to the pyridyl donor, which is the same as in the structures of the isoelectronic group 5 compounds [M(NR)(N_2N_{py})Cl(py)] (M = Nb or Ta).[12] The $N_{pyridyl}-W-N_{imide}$ angle is somewhat less than linear, being 165.89(7)°. The $W-N_{imide}-C$ bond angle is 164.8(2)° indicating that the imido ligand is able in principle to function as a 4-electron donor. The N_{amide} atoms are sp^2 hybridized, adopting an approximate trigonal planar geometry (sum of angles subtended at N(2) = 358.3(4)°; sum of angles subtended at N(3) = 359.9(4)°), implying that the N_{amide}

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(10) Boncella, J. M.; Wang, S. S.; VanderLende, D. D.; Huff, R. L.; Abboud, K. A.; Vaughan, W. M. *J. Organomet. Chem.* **1997**, *530*, 59.

(11) Wang, S. S.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 11990.

(12) Pugh, S. M.; Blake, A. J.; Gade, L. H.; Mountford, P. *Inorg. Chem.* **2001**, *40*, 3992.

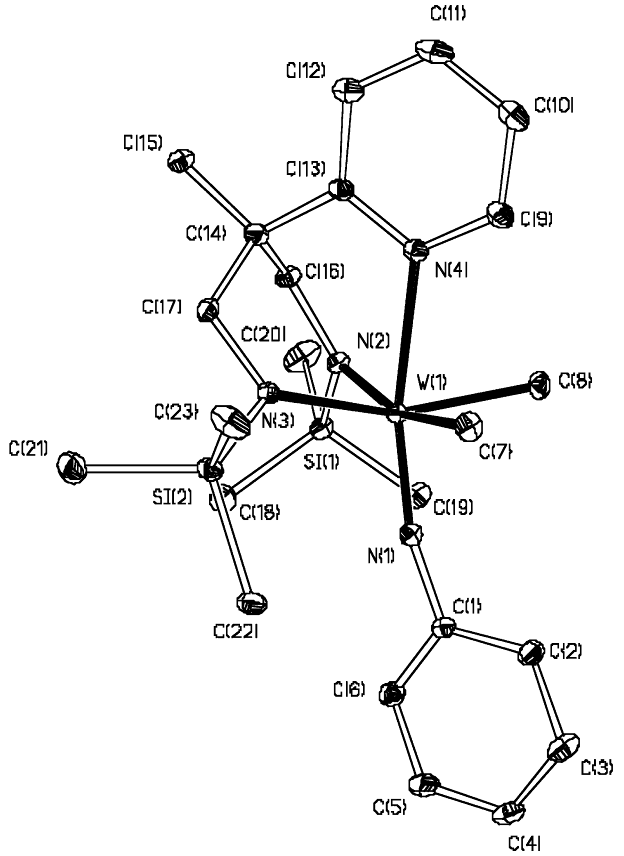

Figure 2. Molecular structure of $[W(NPh)(N_2N_{py})Me_2]$ (**5**). Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[W(NPh)(N_2N_{py})Me_2]$ (**5**)

W(1)−N(1)	1.745(2)	W(1)−N(4)	2.336(2)
W(1)−N(2)	1.997(2)	W(1)−C(7)	2.250(2)
W(1)−N(3)	2.042(2)	W(1)−C(8)	2.228(2)
C(7)−W(1)−C(8)	87.06(8)	W(1)−N(2)−Si(1)	122.36(9)
N(1)−W(1)−N(4)	165.89(7)	W(1)−N(2)−C(16)	122.26(14)
N(2)−W(1)−N(3)	88.61(7)	Si(1)−N(2)−C(16)	113.63(14)
N(3)−W(1)−C(7)	86.40(7)	W(1)−N(3)−Si(2)	127.9(1)
N(2)−W(1)−C(8)	91.97(8)	W(1)−N(3)−C(17)	119.53(13)
W(1)−N(1)−C(1)	164.8(2)	Si(2)−N(3)−C(17)	112.51(13)

functions can, in principle, donate 3 electrons each to the metal center. In practice, if this were the case, a 20 valence electron compound would be formed. This is a "π-loaded" system with 4 ligand π-donor orbitals and 3 metal (t_{2g}-like) π-acceptor orbitals. Therefore, one of the N_{amide} lone pairs is probably based in a nonbonding orbital, with each N_{amide} donating an average of 2 electrons, just as proposed for the isoelectronic group 5 compounds $[M(NR)(N_2N_{py})Cl(py)]$.[12]

The $W-N_{imide}$ bond length of 1.745(2) Å is within the range of values reported in the literature (1.610−2.205, mean 1.762 Å for 173 examples).[13,14] Likewise, the W−C distances of 2.250(2) and 2.228(2) Å are within the range for previously reported compounds (2.009−2.616, mean 2.366 Å for 365 examples). The $W-N_{pyridyl}$ bond length of 2.336(2) Å and $W-N_{amide}$ bond lengths of 1.997(2) and 2.042(2) Å are within previously reported ranges ($W-N_{pyridine}$ = 2.071−2.576, mean 2.255 Å for 243 examples; $W-N_{amide}$ = 1.828−2.480, mean 2.032 Å for 179 examples).

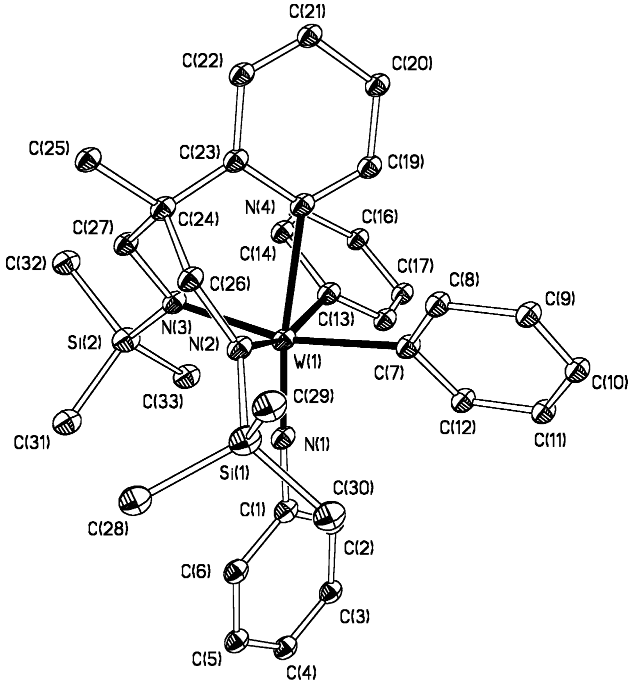

Figure 3. Molecular structure of $[W(NPh)(N_2N_{py})Ph_2]$ (**6**). Displacement ellipsoids are drawn at the 25% probability level. H atoms omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of $[W(NPh)(N_2N_{py})Ph_2]$ (**6**)

W(1)−N(1)	1.77(2)	W(1)−N(4)	2.302(13)
W(1)−N(2)	2.00(2)	W(1)−C(7)	2.20(2)
W(1)−N(3)	2.03(2)	W(1)−C(13)	2.21(2)
C(7)−W(1)−C(13)	91.1(5)	W(1)−N(2)−Si(1)	127.1(8)
W(1)−N(1)−C(1)	175.4(14)	W(1)−N(2)−C(26)	122.7(12)
N(3)−W(1)−C(13)	88.7(6)	Si(1)−N(2)−C(26)	110.1(11)
N(2)−W(1)−C(7)	87.8(5)	W(1)−N(3)−Si(2)	125.0(8)
N(2)−W(1)−N(3)	87.6(6)	W(1)−N(3)−C(27)	120.7(10)
N(1)−W(1)−N(4)	171.6(6)	Si(2)−N(3)−C(27)	113.9(11)

The X-ray structure of $[W(NPh)(N_2N_{py})Ph_2]$ (**6**) was also determined and is similar to that of **5**. The molecular structure of **6** is shown in Figure 3, and selected bond lengths and angles are shown in Table 4. Although the crystals of **6** were poor diffractors, a satisfactory anisotropic refinement was achieved subject to loose vibrational restraints to most non-H atoms, planarity restraints on the phenyl and pyridyl rings, and similarity restraints on the internal angles of the C(1)−C(6) ring. For this reason, it is inappropriate to comment on particular bond lengths and angles to a high precision, and consequently, a detailed comparison with the molecular structure of **5** cannot be made. In general terms, however, it is clear that compound **6** (like **5**) possesses a distorted octahedral geometry about the tungsten center. The $N_{pyridyl}-W-N_{imide}$ angle of 171.6(6)° appears somewhat more linear than that in **5** (165.89(7)°). The angle subtended at the N_{imide} (175.4(14)°) is evidently larger than the corresponding angle observed in **5** (164.8(2)°). This increase in linearity of the imido linkage can be rationalized by considering the greater steric bulk imposed by a phenyl group versus a methyl group. The N_{amide} moieties are sp^2 hybridized, as inferred from their

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(13) Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 1 and 31.

(14) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

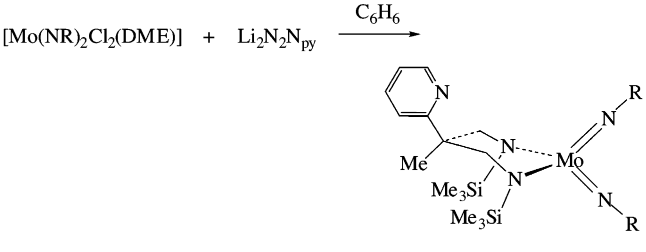
trigonal planar geometry (sum of angles subtended at N(2) = 359.9(31)°; sum of angles subtended at N(3) = 359.6(29)°). The W−C bond lengths in **9** (2.20(2) and 2.21(2) Å) are within the range of values observed previously (2.065−2.330, mean 2.168 Å for 63 examples).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of [W(NPh)(N_2N_{py})Me_2] (**5**) are essentially identical to those of [W(NPh)(N_2N_{py})Cl_2] (**1**) and indicate C_s molecular symmetry with a κ^3-coordinated N_2N_{py} moiety as confirmed by the solid state structure. In addition to the resonances discussed for **1**, the ^{1}H NMR spectrum of **5** exhibits a singlet at 0.77 ppm attributable to the W−Me ligands. Associated ^{183}W satellites were observed with a total integration of ca.15% of the total signal (^{183}W $I = {}^1/_2$, 14.5% abundance), and ^2J(WH) of 5.4 Hz. This value for ^2J(WH) is comparable to previously reported values for diamide-supported tungsten(VI) imido alkyl complexes.[10] The ^{13}C{^{1}H} NMR spectrum showed a resonance for the W−Me ligand at 38.8 ppm, but the ^{183}W satellites were not observed for the natural ^{13}C abundance compound. The ^1J(WC) coupling constant of 71 Hz was determined from the ^{13}C{^{1}H} NMR spectrum of **5-^{13}C$_2$**.

In contrast to the ^{1}H NMR spectrum of **5**, that of [W(NPh)(N_2N_{py})Ph_2] (**6**), featuring for example two inequivalent $SiMe_3$ environments, is consistent with a C_1 molecular symmetry in solution. A single H^6 proton resonance is observed at 9.08 ppm, suggesting that the pyridyl donor is coordinated to the metal center and that only one compound is present in solution. The ^{13}C{^{1}H} NMR spectrum of **6** also indicates C_1 symmetry. The molecular symmetry implied by the NMR spectra of **6** is inconsistent with the solid state structure, which possesses approximate C_s symmetry. It is unclear why this should be the case, but one possible explanation is that in solution an isomer having the phenylimido group *cis* to the pyridyl donor and one of the phenyl ligands *trans* is formed. The synthesis of a bis(*p*-tolyl) derivative was attempted to clarify the situation, but no tractable product was obtained.

Mono(imido) molybdenum compounds analogous to the tungsten compounds already discussed could not be prepared by analogous methods employed for the tungsten systems due to the unavailability of suitable mono(imido) precursors. Therefore, a preparative procedure analogous to that employed by Boncella et al. was attempted, namely by protonolysis of a bis(imido) compound of the form [Mo(NR)$_2$Cl$_2$(DME)] (R = ^{t}Bu, Ph), thereby eliminating 1 equiv of the corresponding primary amine RNH_2 to afford a mono(imido) complex [Mo(NR)(N_2N_{py})Cl_2].[15] Unfortunately, all attempts were unsuccessful, presumably due to the fact that the $H_2N_2N_{py}$ ligand is not sufficiently Brønsted acidic to remove an imido group by protonolysis. Similar attempts using the (presumably) more N−H Brønsted acidic N-aryl substituted protio-ligands MeC(2-C_5H_4N){CH_2NH(4-C_6H_4-Me)}$_2$ and MeC(2-C_5H_4N){CH_2NH(2,4,6-$C_6H_2Me_3$)}$_2$ were also unsuccessful, each giving rise to a complex mixture of products. However, some bis(imido) compounds supported by diamido-donor ligands were prepared via reaction of the bis(imido) precursors [Mo(NR)$_2$Cl$_2$(DME)] (R = ^{t}Bu, Ph) with the dilithium amides $Li_2N_2N_{py}$ and $Li_2N_2N_{am}$.

Reaction of $Li_2N_2N_{py}$ with [Mo(N^{t}Bu)$_2$Cl$_2$(DME)][16] in benzene afforded the four-coordinate bis(imido) compound [Mo(N^{t}Bu)$_2$(N_2N_{py})] (**7**, eq 5) in high yield as a yellow oil which crystallized on standing for 18 h. An attempt to determine the solution molecular weight of **7** by vapor diffusion methods suggested that the compound is monomeric in solution. Attempts to prepare a mono(imido) species [Mo(NR)(N_2N_{py})Cl_2] by subsequent reaction of **7** with various sources of HCl (e.g., quaternary ammonium salts) resulted only in the formation of the protio-ligand $H_2N_2N_{py}$ and unidentified molybdenum-containing species.



R = ^{t}Bu (**7**) or Ph (**8**)

The ^{1}H and ^{13}C{^{1}H} NMR spectra of [Mo(N^{t}Bu)$_2$(N_2N_{py})] (**7**) are consistent with molecular C_s symmetry with equivalent $SiMe_3$ groups but inequivalent ^{t}Bu groups. The difference ($\Delta\delta$) between the chemical shifts of ^{t}Bu methyl- and quaternary-carbons is $\Delta\delta = 34.8$ and 34.7 ppm, indicating a reasonably electrophilic metal center.[17] The ^{1}H NMR spectrum features a signal at 8.51 ppm, assigned to the pyridyl H^6 proton. The chemical shift of this resonance suggests that the pyridyl group is not coordinated, the shift being comparable to that of free $H_2N_2N_{py}$ as well as to those of group 4 and 5 imido compounds containing κ^2-coordinated N_2N_{py} ligands (all in C_6D_6).[12,18]

The NMR spectra of **7** alone do not rule out a dimeric structure with bridging imido ligands, namely [Mo$_2$(N^{t}Bu)$_2$(N_2N_{py})$_2$(μ-N^{t}Bu)$_2$]. Indeed, both monomeric[19] and dimeric[20] bis(imido) compounds of this type are known. Additionally, Boncella has reported an apparently related dimeric compound [Mo$_2$(NPh)$_2${*o*-(Me$_3$Si)$_2$C$_6$H$_4$}$_2$(μ-NPh)$_2$].[15] It is thought, however, that the increased steric bulk imposed by the N^{t}Bu groups in **7** causes the compound to adopt a monomeric structure.

The reaction of $Li_2N_2N_{py}$ with [Mo(NPh)$_2$Cl$_2$(DME)][21] (eq 5) afforded the compound [Mo(NPh)$_2$(N_2N_{py})], **8**, as a waxy

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(15) Ortiz, C. G.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1999**, *18*, 4253.

(16) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, *14*, 103.

(17) Pugh, S. M.; Trösch, D. J. M.; Wilson, D. J.; Bashall, A.; Cloke, F. G. N.; Gade, L. H.; Hitchcock, P. B.; McPartlin, M.; Nixon, J. F.; Mountford, P. *Organometallics* **2000**, *19*, 3205.

(18) Blake, A. J.; Collier, P. E.; Gade, L. H.; Mountford, P.; Pugh, S. M.; Schubart, M.; Skinner, M. E. G.; Trösch, D. J. M. *Inorg. Chem.* **2001**, *40*, 870.

(19) Hursthouse, M. B.; Motevalli, M.; Sullivan, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1398.

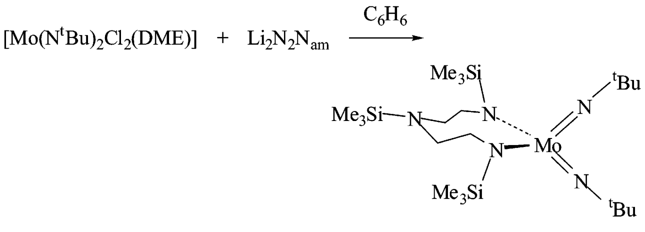
(20) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759.

(21) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.

brown solid. The ^{1}H NMR spectrum of the product revealed the presence of the protio-ligand $H_2N_2N_{py}$ as an impurity, but all attempts to purify the compound were unsuccessful. The presence of protio-ligand (which arises even in NMR tube scale experiments using rigorously dried C_6D_6) has been attributed to redox side-reactions occurring in the Mo(VI) system.

The room temperature ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **8** differ from those of **7** in that they imply C_{2v} symmetry on the NMR time scale, with the phenyl groups, as well as the $SiMe_3$ groups, being equivalent. This could be attributable to a fast monomer−dimer equilibrium (with either a monomeric or dimeric resting state). A dimer such as $[Mo_2(NPh)_2(N_2N_{py})_2(\mu\text{-}NPh)_2]$ could, in principle, dissociate into monomeric compounds $[Mo(NPh)_2(N_2N_{py})]$ (and vice versa). Subsequent reassociation of the monomer would interconvert the terminal and bridging imido ligands, giving a time averaged signal in the NMR spectra showing the two phenyl environments as equivalent. Low temperature NMR experiments were carried out but were inconclusive. For this reason, we depict **8** as a monomeric compound in eq 5, although a dimeric strucuture is also feasible. A monomer−dimer equilibrium is more likely for compound **8** than for compound **7** since the NPh ligands are less sterically demanding than the N^{t}Bu ligands. As noted, Boncella has reported previously the phenylimido-bridged, dimeric compound $[Mo_2(NPh)_2\{o\text{-}(Me_3Si)_2C_6H_4\}_2(\mu\text{-}NPh)_2]$.[15]

The lithiated diamido-amine $Li_2N_2N_{am}$ reacts with $[Mo(N^tBu)_2Cl_2(DME)]$ to afford the compound $[Mo(N^tBu)_2(N_2N_{am})]$, **9**, as a brown oil (eq 6). The oil was highly soluble in aliphatic solvents such as pentane, and attempts to purify the compound by sublimation or distillation led only to decomposition. Consequently, an analytically pure sample could not obtained but, on the basis of available data and the proposed structure of **7**, is assigned a monomeric structure.



9

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of $[Mo(N^tBu)_2(N_2N_{am})]$, **9**, indicate C_{2v}-symmetry on the NMR time scale with equivalent amide-$SiMe_3$ and N^{t}Bu groups. The carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum give $\Delta\delta$ as 34.9 ppm. The observed C_{2v} symmetry suggests that N^{t}Bu ligands can interconvert on the NMR time scale. This can be achieved by facile and rapid inversion at the tertiary amine nitrogen of the N_2N_{am} ligand, which gives a time averaged signal corresponding to apparent C_{2v} molecular symmetry (an equivalent process is not possible for the N_2N_{py} ligand explaining why **7** possesses C_s symmetry). Inversion at the amine nitrogen of the N_2N_{am} ligand has been observed by Cloke and co-workers in the titanium dialkyl compound $[Ti(N_2N_{am})Me_2]$.[22]

Summary

The synthesis and characterization of a series of tungsten imido-dichloride compounds supported by diamido-donor ligands, and the subsequent reaction of $[W(NPh)(N_2N_{py})Cl_2]$, **1**, with Grignard reagents to afford the corresponding dialkyl compounds $[W(NPh)(N_2N_{py})R_2]$ (R = Me, **5**, or Ph, **6**), have been described. This contrasts with the imido-diamide group 6 systems of Boncella and co-workers for which a range of different dialkyl derivatives may be obtained.[5] The analogous molybdenum compounds have proved to be inaccessible, again in contrast to Boncella's systems. Three examples of diamide-supported molybdenum bis(imido) compounds have been prepared, of which only $[Mo(N^tBu)_2(N_2N_{py})]$, **2**, has been isolated in a pure form due to adverse effects of high solubility and redox side-reactions. Investigations into the reactivity of cationic tungsten monomethyl compounds derived from **5** are currently underway.[6]

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Solvents were predried over activated 4 Å molecular sieves and were refluxed over potassium (tetrahydrofuran, benzene, dimethoxyethane, hexanes), sodium/potassium alloy (pentane), sodium (toluene), or sodium/benzophenone (diethyl ether) under a dinitrogen atmosphere and collected by distillation. Deuterated solvents were dried over potassium (C_6D_6, toluene-d_8), distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^{1}H and ^{13}C assignments were confirmed when necessary with the use of DEPT-135, DEPT-90, and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR experiments. ^{1}H and ^{13}C spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as KBr pellets or Nujol mulls between KBr plates and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers. Infrared data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of the University of Oxford Inorganic Chemistry Laboratory or Dyson Perrins Laboratory, and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory.

Literature Preparations. The compounds $[W(NPh)Cl_4(THF)]$,[23] $[W(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_4(THF)]$,[24] $[Mo(N^tBu)_2Cl_2(DME)]$,[16] $[Mo(NPh)_2Cl_2(DME)]$,[21] $Li_2N_2N_{py}$,[7] $MeC(2\text{-}C_5H_4N)\{CH_2NH(4\text{-}C_6H_4\text{-}Me)\}_2$,[4] $MeC(2\text{-}C_5H_4N)\{CH_2NH(2,4,6\text{-}C_6H_2Me_3)\}_2$, $Li_2N_2N_{am}$,[26]

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(22) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333.

(23) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651.

(24) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130.

(25) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841.

$LiCH_2SiMe_3$,[27] and PhLi[28] were prepared according to published methods. $^{13}CH_3MgI$ was prepared using standard methods.[29] All other compounds and reagents were purchased from commercial chemical suppliers and used without further purification.

[W(NPh)(N_2N_{py})Cl_2] (1). To a stirred solution of [W(NPh)Cl_4(THF)] (300 mg, 0.614 mmol) in benzene (20 mL) cooled to 7 °C was added a cooled (7 °C) solution of $Li_2N_2N_{py}$ (197 mg, 0.614 mmol, 1 equiv) in benzene (20 mL) dropwise over ca. 15 min. The resulting dark red mixture was allowed to warm to room temperature and stirred for a further 1 h before filtering away from the LiCl and subsequently removing the volatiles under reduced pressure. The resulting brown solid was washed with pentane (3 × 20 mL) before drying in vacuo to yield [W(NPh)(N_2N_{py})Cl_2] as a dark red solid. Yield: 337 mg (84%).

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 10.27 (1 H, dd, $^3J(H^5H^6) = 5.9$ Hz, $^4J(H^4H^6) = 1.5$ Hz, H^6), 7.81 (2 H, d, $^3J = 7.8$ Hz, *o*-C_6H_5), 7.22 (2 H, t, $^3J = 7.8$ Hz, *m*-C_6H_5), 6.92 (1 H, td, $^3J(H^3H^4H^5) = 7.7$ Hz, $^4J(H^4H^6) = 1.5$ Hz, H^4), 6.74 (1 H, t, $^3J = 7.8$ Hz, *p*-C_6H_5), 6.67 (1 H, d, $^3J(H^3H^4) = 7.9$ Hz, H^3), 6.51 (1 H, td, $^3J(H^4H^5H^6) = 6.8$ Hz, $^4J(H^3H^5) = 1.1$ Hz, H^5), 3.82 (4 H, overlapping d, $^2J = 13.5$ Hz, CH_2NSiMe_3), 0.92 (3 H, s, Me of N_2N_{py}), 0.29 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 125.7 MHz, 293 K): 160.5 (C^2), 154.7 (C^6), 139.9 (*ipso*-C_6H_5), 128.4 (*o*-C_6H_5), 128.3 (*m*-C_6H_5), 127.5 (*p*-C_6H_5), 126.5 (C^4), 122.7 (C^5), 117.3 (C^3), 62.1 (CH_2NSiMe_3), 49.9 ($C(CH_2NSiMe_3)_2$), 20.8 (Me of N_2N_{py}), −0.3 ($SiMe_3$). EI-MS: $m/z = 654$ (1%) $[M]^+$, 639 (2%) $[M - Me]^+$, 584 (2%) $[M - 2Cl]^+$. IR data (KBr plates, Nujol, cm^{-1}): 2860 (s), 1640 (m), 1610 (m), 1595 (m), 1495 (m), 1260 (m), 1255 (m), 1040 (m), 920 (w), 840 (m), 810 (m), 695 (w), 620 (w). Found (Calcd for $C_{21}H_{34}Cl_2N_4Si_2W$): C 38.3 (38.6), H 4.6 (5.2), N 8.6 (8.6)%.

[W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] (2). To a stirred solution of [W(N-2,6-$C_6H_3Me_2$)Cl_4(THF)] (200 mg, 0.39 mmol) in cold (7 °C) benzene (20 mL) was added a solution of $Li_2N_2N_{py}$ (125 mg, 0.39 mmol, 1 equiv) in cold (7 °C) benzene dropwise over ca. 15 min. The reaction was allowed to warm to room temperature and stirred for a further 2 h. The precipitated LiCl was removed by filtration, and the volatiles were removed under reduced pressure. The product was extracted with hexanes (2 × 10 mL) and filtered away from the insoluble impurities. The dark red solution was concentrated and cooled to −80 °C. [W(N-2,6-$C_6H_3Me_2$)(N_2N_{py})Cl_2] was collected as a dark red solid after 48 h. Yield: 21 mg (8%).

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 10.03 (1 H, d, $^3J(H^6H^5) = 5.5$ Hz, H^6), 6.97 (2 H, d, $^3J = 7.3$ Hz, *m*-$C_6H_3Me_2$), 6.87 (1 H, td, $^3J(H^3H^4H^5) = 7.7$ Hz, $^4J(H^4H^6) = 1.8$ Hz, H^4), 6.65 (1 H, overlapping m, H^3), 6.60 (1 H, overlapping m, *p*-$C_6H_3Me_2$), 6.45 (1 H, td, $^3J(H^4H^5H^6) = 6.2$ Hz, $^4J(H^3H^5) = 1.1$ Hz, H^5), 3.84 (4 H, s, CH_2), 3.61 (3 H, s, $C_6H_3Me_2$), 2.67 (3 H, s, $C_6H_3Me_2$), 0.95 (3 H, s, Me of N_2N_{py}), 0.21 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 125.7 MHz, 293 K): 160.5 (C^2), 153.4 (*ipso*-$C_6H_3Me_2$), 140.7 (*o*-$C_6H_3Me_2$), 139.1 (C^6), 132.5 (*o*-$C_6H_3Me_2$), 128.5 (*m*-$C_6H_3Me_2$), 128.2 (*m*-$C_6H_3Me_2$), 127.1 (*p*-$C_6H_3Me_2$), 126.3 (C^4), 122.2 (C^5), 116.9 (C^3), 63.4 (CH_2NSiMe_3), 51.5 ($C(CH_2NSiMe_3)_2$), 21.7 (Me of N_2N_{py}), 19.7 ($C_6H_3Me_2$), 17.8 ($C_6H_3Me_2$), 0.3 ($SiMe_3$). IR data (KBr plates, Nujol, cm^{-1}): 3331 (m), 3259 (m), 2727 (m), 1304 (w), 1261 (m), 1154 (w), 1094 (m, br), 1020 (m, br), 841 (w), 801 (m), 723 (s), 424 (s). Found (Calcd for $C_{23}H_{38}Cl_2N_4Si_2W$): C 41.6 (40.5), H 5.1 (5.6), N 7.9 (8.2)%.

[W(NPh)(N_2N_{am})Cl_2] (3). To a stirred solution of [W(NPh)Cl_4(THF)] (250 mg, 0.51 mmol) in benzene (20 mL) cooled to 7 °C was added a solution of $Li_2N_2N_{am}$ (170 mg, 0.51 mmol, 1 equiv) in benzene (20 mL) dropwise over ca. 15 min. The reaction was allowed to warm to ambient temperature and stirred for a further 1 h. The precipitated LiCl was removed by filtration and the filtrate concentrated to dryness in vacuo. The brown solid was extracted with hexanes (2 × 10 mL), filtered away from insoluble impurities. The filtrate was concentrated and cooled to −80 °C for 48 h to give [W(NPh)(N_2N_{am})Cl_2] as a golden brown solid. Yield: 100 mg (29%).

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 7.66 (2 H, d, $^3J = 7.5$ Hz, *o*-C_6H_5), 7.06 (2 H, t, $^3J = 7.5$ Hz, *m*-C_6H_5), 6.69 (1 H, t, $^3J = 7.5$ Hz, *p*-C_6H_5), 4.04 (2 H, m, CHH), 3.92 (2 H, m, CHH), 3.39 (2 H, m, CHH), 2.34 (2 H, m, CHH), 0.46 (9 H, s, amine-$SiMe_3$), 0.29 (18 H, s, amide-$SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 154.0 (*ipso*-C_6H_5), 124.4 (*o*-C_6H_5), 128.1 (*m*-C_6H_5), 127.4 (*p*-C_6H_5), 56.3 (CH_2), 54.7 (CH_2), 2.0 (amide-$SiMe_3$), 0.5 (amine-$SiMe_3$). EI-MS: $m/z = 662$ (1%) $[M]^+$, 627 (10%) $[M - Cl]^+$, 593 (8%) $[M - 2Cl]^+$. IR data (KBr plates, Nujol, cm^{-1}): 2686 (w), 1732 (w), 1714 (w), 1332 (w), 1254 (m), 1072 (w), 1028 (m), 938 (w), 904 (w), 872 (m), 840 (m), 796 (m), 762 (w), 722 (w), 684 (w), 634 (w). Found (Calcd for $C_{19}H_{40}Cl_2N_4Si_3W$): C 35.1 (34.4), H 7.1 (6.1), N 9.3 (8.4)%.

[W(N-2,6-$C_6H_3Me_2$)(N_2N_{am})Cl_2] (4). To a stirred solution of [W(N-2,6-$C_6H_3Me_2$)Cl_4(THF)] (500 mg, 0.97 mmol) in cold (7 °C) benzene (20 mL) was added a solution of $Li_2N_2N_{am}$ (192 mg, 0.97 mmol, 1 equiv) in cold (7 °C) benzene dropwise over ca. 15 min. The reaction was allowed to warm to room temperature and stirred for a further 1 h. The volatiles were removed under reduced pressure to yield a brown solid. The crude product was extracted with hexanes, and the resulting brown solution was filtered away from the insoluble residues. The combined extracts were concentrated and cooled to −80 °C. [W(N-2,6-$C_6H_3Me_2$)(N_2N_{am})Cl_2] was collected as a golden brown solid after 7 days. Yield: 98 mg (15%) in 2 crops.

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 6.85 (2 H, d, $^3J = 7.6$ Hz, *m*-$C_6H_3Me_2$), 6.59 (1 H, t, $^3J = 7.6$ Hz, *p*-$C_6H_3Me_2$), 4.14 (2 H, m, CHH), 4.00 (2 H, m, CHH), 3.52 (2 H, m, CHH), 2.98 (6 H, s, $C_6H_3Me_2$), 2.36 (2 H, dd, $^3J = 4.0$ Hz, $^2J = 12.2$ Hz, CHH), 0.45 (9 H, s, amine-$SiMe_3$), 0.22 (18 H, s, amide-$SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 152.7 (*ipso*-$C_6H_3Me_2$), 138.7 (*o*-$C_6H_3Me_2$), not observed (*m*-$C_6H_3Me_2$), 127.8 (*p*-$C_6H_3Me_2$), 56.9 (CH_2), 55.5 (CH_2), 19.8 ($C_6H_3Me_2$), 1.2 (amide-$SiMe_3$), 0.6 (amine-$SiMe_3$). EI-MS: $m/z = 692$ (3%) $[M]^+$, 657 (20%) $[M - Cl]^+$, 621 (8%) $[M - 2Cl]^+$, 481 (75%) $[M - Cl - N(SiMe_3)(CH_2)(CH_2CH_2) - 3Me]^+$. IR data (KBr plates, Nujol, cm^{-1}): 2692 (w), 1318 (w), 1298 (w), 1252 (m), 1064 (m), 1022 (m), 938 (w), 916 (w), 870 (m), 840 (m), 798 (m), 754 (w), 722 (w), 694 (w), 632 (w), 544 (w). Found (Calcd for $C_{21}H_{44}Cl_2N_4Si_3W$): C 37.2 (36.5), H 6.5 (6.4), N 8.1 (8.1)%.

[W(NPh)(N_2N_{py})Me_2] (5). [W(NPh)(N_2N_{py})Cl_2] (**1**) (600 mg, 0.92 mmol) was dissolved in benzene (30 mL) and cooled to 7 °C. To this dark red solution was added MeMgBr (1.31 mL of a 1.4 M solution in 1:3 THF/toluene, 1.84 mmol, 2 equiv) dropwise. The reaction was allowed to warm to ambient temperature. After stirring for a further 2 h, 1,4-dioxane (1 mL) was added to aid precipitation of the magnesium salts. The precipitated salts were removed by filtration, and the volatiles were removed from the filtrate under reduced pressure. The crude product was extracted with pentane (3 × 20 mL) and the solvent removed from the combined extracts under reduced pressure to yield 165 mg (35%) of [W(NPh)(N_2N_{py})Me_2] as a red crystalline solid. Single crystals suitable for X-ray

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(26) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

(27) Connolly, J. W.; Urry, G. *Inorg. Chem.* **1963**, *2*, 645.

(28) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

(29) Grignard, V. *Ann. Chim. Phys.* **1901**, *24*, 433.

diffraction were grown from a saturated pentane solution. The compounds $[W(NPh)(N_2N_{py})(^{13}CH_3)_2]$ (**5-^{13}C$_2$**) and $[W(NPh)(N_2N_{py})(CD_3)_2]$ (**5-*d*$_6$**) were prepared by analogous methods using $^{13}CH_3MgI$ and CD_3MgI in 34% and 22% yields, respectively.

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 8.91 (1 H, dd, $^3J(H^5H^6) = 5.7$ Hz, $^4J(H^4H^6) = 1.5$ Hz, H^6), 7.54 (2 H, d, $^3J = 7.5$ Hz, *o*-C_6H_5), 7.27 (2 H, t, $^3J = 7.5$ Hz, *m*-C_6H_5), 7.00 (1 H, td, $^3J(H^3H^4H^5) = 7.9$ Hz, $^4J(H^4H^6) = 1.5$ Hz, H^4), 6.85 (1 H, overlapping m, H^3), 6.85 (1 H, overlapping m, *p*-C_6H_5), 6.50 (1 H, m, H^5), 3.39 (4 H, s, CH_2), 1.04 (3 H, s, Me of N_2N_{py}), 0.77 (6 H, s, $^2J(WH) = 5.4$ Hz (15%), WMe_2), 0.25 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 164.5 (C^2), 151.5 (C^6), 138.2 (*o*-C_6H_5), 128.7 (*ipso*-C_6H_5), 127.8 (*m*-C_6H_5), 126.4 (*p*-C_6H_5), 125.3 (C^4), 121.7 (C^5), 118.1 (C^3), 61.9 ($\textit{C}H_2NSiMe_3$), 52.5 ($\textit{C}(CH_2NSiMe_3)_2$), 38.8 ($^1J(CH) = 120.5$ Hz, $^1J(WC) = 71$ Hz (15%), WMe_2), 22.8 (Me of N_2N_{py}), 1.8 ($SiMe_3$). EI-MS: $m/z = 612.6$ (1%) $[M]^+$, 597.5 (30%) $[M - Me]^+$. IR data (KBr plates, Nujol, cm^{-1}): 2726 (w), 2336 (w), 1732 (w), 1588 (m), 1256 (m), 1026 (w), 914 (m), 840 (m), 804 (w), 724 (w), 690 (w). Found (Calcd for $C_{23}H_{40}N_4Si_2W$): C 44.5 (45.1), H 6.5 (6.6), N 9.1 (9.2)%.

$[W(NPh)(N_2N_{py})Ph_2]$ (6). $[W(NPh)(N_2N_{py})Cl_2]$ (**1**) (200 mg, 0.31 mmol) was dissolved in benzene and cooled to 7 °C. To this stirred solution was added PhMgCl (0.31 mL of a 2.0 M solution in THF, 0.62 mmol, 2 equiv) dropwise. The solution was allowed to warm to ambient temperature and stirred for a further 2 h before adding 1,4-dioxane (1 mL) to aid salt precipitation. The reaction was filtered to remove magnesium salts, and the resulting dark red solution was concentrated to dryness under reduced pressure. The product was extracted into pentane (50 mL) and filtered, and the volatiles were removed in vacuo to yield $[W(NPh)(N_2N_{py})Ph_2]$ as a red solid. Yield: 52 mg (23%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution.

^{1}H NMR data (C_6D_6, 300.1 MHz, 293 K): 9.08 (1 H, dd, $^3J(H^5H^6) = 8.7$ Hz, $^4J(H^4H^6) = 0.8$ Hz, H^6), 8.22 (2 H, br s, C_6H_5), 7.84 (2 H, d, $^3J = 7.4$ Hz, C_6H_5), 7.45 (2 H, dd, $^3J = 8.6$ Hz, $^4J = 1.7$ Hz, C_6H_5), 7.26−7.08 (7 H, overlapping m, H^3, C_6H_5), 6.89−6.71 (4 H, overlapping m, H^4, C_6H_5), 6.13 (1 H, td, $^3J(H^4H^5H^6) = 8.7$ Hz, $^4J(H^3H^5) = 0.8$ Hz, H^5), 3.92−3.65 (4 H, overlapping m, CH_2), 1.02 (3 H, s, Me of N_2N_{py}), 0.33 (9 H, s, $SiMe_3$), 0.12 (9 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 193.5 (*ipso*-W−C_6H_5), 161.6 (C^2), 155.5 (C^6), 154.8 (*ipso*-N−C_6H_5), 142.6 (C_6H_5), 141.7 (C_6H_5), 139.1 (*o*-N−C_6H_5), 129.0 (C^4), 127.4 (*m*-N−C_6H_5), 126.8 (*p*-N−C_6H_5), 126.1 (C^5), 125.0 (C_6H_5), 121.7 (C_6H_5), 117.6 (C^3), 63.9 ($\textit{C}H_2NSiMe_3$), 62.9 ($\textit{C}H_2NSiMe_3$), 51.6 ($\textit{C}(CH_2NSiMe_3)_2$), 22.5 (Me of N_2N_{py}), 1.7 ($SiMe_3$), 1.6 ($SiMe_3$). EI-MS: $m/z = 736$ (10%) $[M]^+$, 659 (100%) $[M - C_6H_5]^+$, 646 (50%) $[M - NC_6H_5)]^+$. IR data (KBr plates, Nujol, cm^{-1}): 3751 (w), 3649 (w), 1261 (s), 839 (s), 802 (m), 723 (m). Found (Calcd for $C_{33}H_{44}N_4Si_2W$): C 48.6 (53.8), H 6.2 (6.0), N 7.3 (7.6)%.

$[Mo(N^tBu)_2(N_2N_{py})]$ (7). To a stirred solution of $[Mo(N^tBu)_2Cl_2(DME)]$ (500 mg, 1.26 mmol) in benzene (10 mL) was added a solution of $Li_2N_2N_{py}$ (405 mg, 1.26 mmol, 1 equiv) in benzene (10 mL) dropwise over ca. 15 min. During the addition, the clear yellow solution became cloudy. The reaction was stirred for a further 1 h before filtering away from the precipitated LiCl. The solvent was removed in vacuo to give a yellow oil which crystallized overnight to give $[Mo(N^tBu)_2(N_2N_{py})]$ as a yellow solid. Yield: 590 mg (86%).

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K): 8.51 (1 H, dd, $^3J(H^5H^6) = 4.0$ Hz, $^4J(H^3H^6) = 1.1$ Hz, H^6), 7.17 (1 H, overlapping m, H^3), 7.08 (1 H, overlapping m, H^4), 6.58 (1 H, overlapping m, H^5), 4.75 (2 H, d, $^2J = 15.0$ Hz, $C\textit{H}H$), 3.75 (2 H, d, $^2J = 15.0$ Hz, $CH\textit{H}$), 1.52 (9 H, s, CMe_3), 1.46 (9 H, s, CMe_3), 1.19 (3 H, s, Me of N_2N_{py}), 0.24 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 166.4 (C^2), 149.2 (C^6), 135.7 (C^4), 120.9 (C^5), 120.8 (C^3), 68.2 ($\textit{C}Me_3$), 68.0 ($\textit{C}Me_3$), 63.5 ($\textit{C}H_2SiMe_3$), 47.8 ($\textit{C}(CH_2SiMe_3)_2$), 33.4 ($C\textit{Me}_3$), 33.3 ($C\textit{Me}_3$), 19.8 (Me of N_2N_{py}), 2.2 ($SiMe_3$). IR data (KBr plates, Nujol, cm^{-1}): 2728 (w), 1732 (w), 1378 (m), 1354 (m), 1248 (m), 1206 (m), 1038 (m), 744 (w), 722 (w). Found (Calcd for $C_{23}H_{47}MoN_5Si_2$): C 50.1 (50.6), H 8.7 (8.7), N 12.8 (12.8)%.

$[Mo(NPh)_2(N_2N_{py})]$ (8). To a stirred solution of $[Mo(NPh)_2Cl_2(DME)]$ (250 mg, 0.57 mmol) in benzene (10 mL) was added a solution of $Li_2N_2N_{py}$ (183 mg, 0.57 mmol, 1 equiv) in benzene (10 mL). The reaction was stirred overnight before removing the precipitated LiCl by filtration and removing the voltiles under reduced pressure. The brown sticky solid was dissolved in diethyl ether and cooled to −30 °C to yield $[Mo(NPh)_2(N_2N_{py})]$ as a brown sticky solid, which could not be separated from $H_2N_2N_{py}$. Yield: 263 mg (79%).

^{1}H NMR data (C_6D_6, 300.2 MHz, 293 K):, 8.50 (1 H, d, $^3J(H^5H^6) = 3.7$ Hz, H^6), 7.39 (4 H, dd, $^3J = 7.7$ Hz, $^3J = 16.8$ Hz, *m*-C_6H_5), 7.12 (1 H, d, $^3J(H^3H^4) = 4.8$ Hz, H^3), 7.07 (4 H, d, $^3J = 7.7$ Hz, *o*-C_6H_5), 6.95 (1 H, t, $^3J(H^3H^4H^5) = 4.8$ Hz, H^4), 6.82 (2 H, m, *p*-C_6H_5), 6.62 (1 H, t, $^3J(H^4H^5H^6) = 4.8$ Hz, H^5), 4.92 (2 H, d, $^2J = 15.1$ Hz, $C\textit{H}H$), 3.80 (2 H, d, $^2J = 15.1$ Hz, $CH\textit{H}$), 1.26 (3 H, s, Me of N_2N_{py}), 0.23 (18 H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 165.1 (C^2), 157.6 (*o*-C_6H_5), 149.5 (C^6), 136.0 (C^4), 129.1 (*m*-C_6H_5), 128.9 (*p*-C_6H_5), 124.9 (*ipso*-C_6H_5), 124.2 (C^5), 123.1 (C^3), 50.6 ($\textit{C}H_2NSiMe_3$), 48.4 ($\textit{C}(CH_2NSiMe_3)_2$), 20.4 (Me of N_2N_{py}), 1.8 ($SiMe_3$). Satisfactory elemental analysis was not obtained for this compound due to the presence of free $H_2N_2N_{py}$ redox side-product.

$[Mo(N^tBu)_2(N_2N_{am})]_2$ (9). To a solution of $[Mo(N^tBu)_2Cl_2(DME)$ (200 mg, 0.50 mmol) in benzene (20 mL) cooled to 7 °C was added a solution of $Li_2N_2N_{am}$ (166 mg, 0.50 mmol, 1 equiv) in benzene (20 mL) dropwise over ca. 15 min. The reaction was allowed to warm to ambient temperature and stirred for a further 2 h. The volatiles were removed in vacuo to give a brown oil. The product was extracted into pentane (20 mL), filtered, and concentrated to dryness under reduced pressure to yield a brown oil that was shown by ^{1}H NMR to contain impurities. The oil failed to sublime or distill at 1×10^{-6} mbar (turbomolecular pump-backed high vacuum apparatus). Yield: 264 mg (87%).

^{1}H NMR data (C_6D_6, 300.1 MHz, 293 K): 3.92 (4 H, m, $C\textit{H}H$), 2.79 (4 H, m, $CH\textit{H}$), 1.44 (18 H, s, CMe_3), 0.29 (18 H, s, amide-$SiMe_3$), 0.13 (9 H, s, amine-$SiMe_3$). $^{13}C\{^1H\}$ NMR data (C_6D_6, 75.5 MHz, 293 K): 68.4 ($\textit{C}Me_3$), 64.3 (CH_2), 59.1 (CH_2), 33.5 ($C\textit{Me}_3$), 2.6 (amide-$SiMe_3$), −0.2 (amine-$SiMe_3$). EI-MS: $m/z =$ 1112 (3%) $[M]^+$, 1040 (32%) $[M - NCMe_3]^+$, 556 (80%) $[0.5M]^+$, 485 (35%) $[0.5M - NCMe_3]^+$. IR data (KBr plates, Nujol, cm^{-1}): 2964 (s), 2924 (s), 2898 (s), 2854 (s), 1604 (m), 1450 (m), 1402 (m), 1354 (m), 1244 (s), 1206 (s), 1112 (s), 1062 (s), 982 (s), 910 (s), 838 (s, br), 782 (s), 750 (s), 680 (m), 616 (w), 540 (w), 498 (w), 466 (w). Elemental analysis was not obtained for this compound which was a highly soluble oil.

Crystal Structure Determinations of $[W(NPh)(N_2N_{py})Me_2]$ (5) and $[W(NPh)(N_2N_{py})Ph_2]$ (6). Crystal data collection and processing parameters are given in Table 5. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Kappa-CCD diffractometer equipped with an Oxford Cryosystems low temperature device. Data were collected at low temperature using Mo Kα radiation; equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK

Table 5. X-ray Data Collection and Processing Parameters for [W(NPh)(N_2N_{Py})Me_2] (**5**) and [W(NPh)(N_2N_{Py})Ph_2] (**6**)

	5	**6**
empirical formula	$C_{23}H_{40}N_4Si_2W$	$C_{33}H_{44}N_4Si_2W$
fw	612.62	736.76
temp/K	0.71073	0.71073
wavelength/Å	150	150
space group	$P2_1/n$	$P2_1$
a/Å	10.6452(2)	9.6367(5)
b/Å	16.4633(3)	17.1252(11)
c/Å	15.2794(2)	10.4777(5)
α/deg		
β/deg	91.659(1)	108.144(3)
γ/deg		
V/Å^3	2676.67(8)	1643.2(6)
Z	4	2
d(calcd)/Mg·m^{-3}	1.52	1.49
abs coeff/mm^{-1}	4.42	3.62
R indices R_1, R_w [$I > 3\sigma(I)$]^a	$R_1 = 0.0227$, $R_w = 0.0106$	$R_1 = 0.0642$, $R_w = 0.0683$

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}}$.

programs.[30] Corrections for Lorentz-polarization effects and absorption were performed, and the structures were solved by direct methods using SIR92.[31] Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were placed geometrically unless stated otherwise. Extinction corrections were applied as required.[32] Crystallographic calculations were performed using SIR92[31] and CRYSTALS.[33]

A number of crystals of **6** were examined, and all were found to be poor diffractors. The choice of noncentrosymmetric space group was supported by an examination of the normalized structure factors (SIR92) and successful refinement. However, a satisfactory anisotropic refinement was readily achieved subject to loose vibrational restraints to most non-H atoms, planarity restraints on the phenyl and pyridyl rings, and similarity restraints on the internal angles of the C(1)−C(6) ring.

A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for **5** and **6** have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, issue 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of [W(NAr)(N_2N_{py})Me_2] (**5**) and [W(NAr)(N_2N_{py})Ph_2] (**6**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(31) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(32) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

(33) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I. *CRYSTALS Issue 11*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1997.