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Synthesis of a Square Pyramidal Tungsten(VI) Alkylidene Complex with a Bis(amide) Chelate Ligand

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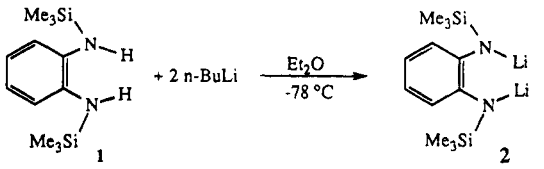
Summary: Reaction of $Li_2[(NSiMe_3)_2C_6H_4]$ *with* $W(NPh)Cl_4(OEt_2)$ *yields* $W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$, ***3****. Compound* ***3*** *can be alkylated to give the corresponding dialkyls,* $W(NPh)R_2[(NSiMe_3)_2C_6H_4]$. $W(NPh)(CH_2CMe_3)_2[(NSiMe_3)_2C_6H_4]$, ***4a****, can be heated in the presence of excess* PMe_3 *to give the new alkylidene complex* $W(NPh)(CHCMe_3)(PMe_3)[(NSiMe_3)_2C_6H_4]$, ***5****. The X-ray structure of* ***5*** *reveals that* ***5*** *adopts a unique square pyramidal structure with the alkylidene carbon in the apical position.*

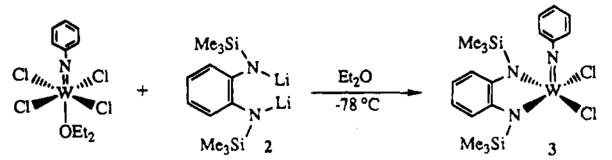
High oxidation state transition metal alkylidene complexes are of great interest because of their ability to catalyze the olefin metathesis reaction, including the polymerization of strained cyclic olefins (ROMP)[1] and acyclic dienes (ADMET).[2] Recent work in our group has led to the synthesis of a new class of chelate stabilized alkylidene complexes that contain derivatives of the hydro(trispyrazolyl)borate ligand.[3] These six-coordinate alkylidene complexes are precursors to active ROMP catalysts when they are activated by Lewis acids.[4] Although their catalytic activity is retained in the air and at elevated temperatures long enough to effect a ROMP reaction or an ADMET oligomerization, long term (over days) catalyst stability is not observed. Furthermore, the catalytically active species in these mixtures are unidentified. Despite these uncertainties, it is evident that the tridentate coordination of the hydrotris(pyrazolyl)borate ligand is responsible for the observed kinetic stability of these complexes as well as the necessity of using Lewis acids as activators. In order to decrease the coordination number of the complexes while retaining the stabilizing effects of the chelate ligand, we have begun to investigate polydentate polyanionic coligands with the metal alkylidene functionality.

Recently, an increasing amount of interest has been focused on the tetradentate ligand $[(RNCH_2CH_2)_3N]^{3-}$, first synthesized by Verkade[5] who initially used it to stabilize five-coordinate main group compounds. This ligand has also been used in a similar fashion with transition metals.[6] The tridentate ligands, $[(RNCH_2CH_2)_3CMe]^{3-}$, have also been synthesized.[7] Since the tetradentate nature of the $[(RNCH_2CH_2)_3N]^{3-}$ ligand will result in the formation of high coordination number complexes with group 6 or 7 metals, we have pursued related ligand systems that are bidentate dianions when coordinated to a metal center. We have focused our attention on a series of sterically encumbered chelating bis(amide) ligands that are derived from N,N′ disubstituted derivatives of *o*-phenylenediamine. In this paper, we report the synthesis, characterization, and X-ray crystal structures of two W(VI) complexes that contain the $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$ ligand system.

The amine $o\text{-}(Me_3SiNH)_2C_6H_4$, **1**, was synthesized in high yield using a slight modification of the literature procedure.[8] Compound **1** can be lithiated (eq 1), and the lithiated amine, **2**, can be isolated, but it is more easily used when generated *in situ* due to its air sensitivity. Addition of 1 equiv of a diethyl ether solution of **2** to $PhN{=}WCl_4(OEt_2)$[9] results in the displacement of two chloride ligands and the formation of **3**, eq 2.[10] Compound **3** was isolated as an air sensitive, rust red powder by removing the ether under reduced pressure and washing the resultant residue with cold pentane. When **3** was exposed to σ-donor ligands such as THF and PMe_3, purple mono adducts were formed. Recrystallization of **3** from toluene gave crystals that were suitable for an X-ray diffraction study.



(1)



(2)

The thermal ellipsoid plot of **3** is found in Figure 1. The coordination geometry about W is a square pyramid with the imido N in the axial position and the [*o*-(Me$_3$-

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(10) Full experimental details for all compounds are given in the supplementary material. $W(NPh)Cl_2[(NSiMe_3)_2C_6H_4]$: Anal. Calcd for $C_{18}H_{27}N_3Cl_2Si_2W$: C, 36.25; H, 4.56; N, 7.05. Found: C, 35.91; H, 4.78; N, 6.78. ^1H NMR (25 °C in C_6D_6): δ 0.35 (s, SiMe$_3$), 6.71 (t, *p*-Ph*H*), 6.94 (m, 2 H), 7.01 (t, *m*-Ph*H*), 7.15 (m, 2 H), 7.31 (d, *o*-Ph*H*).

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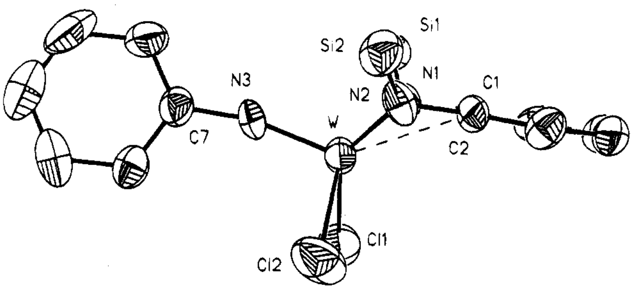
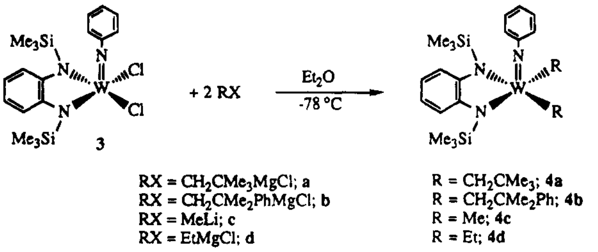


Figure 1. Thermal ellipsoid plot of W(NPh)Cl_2[(NSi-$Me_3)_2C_6H_4$], **3**. The methyl groups have been removed from the silyl groups for clarity. Selected bond distances (Å): W—N(3), 1.730(10); W—N(1), 1.951(11); W—N(2), 1.952(11); N(1)—C(1), 1.42(2); N(2)—C(2), 1.40(2); W—Cl(1), 2.383(4); W—Cl(2), 2.387(4). Selected bond angles (°): C(7)—N-(3)—W, 166.2(9); N(1)—W—N(2), 83.9(4).

$SiN)_2C_6H_4]^{2-}$ ligand and the Cl^- ligands in the basal plane.[11] The W atom sits 0.58 Å above the plane defined by the amide N atoms and the Cl atoms. The W—imido bond length is consistent with a W—N triple bond, as is expected, and gives the compound a formal electron count of 14e. The [o-$(Me_3SiN)_2C_6H_4]^{2-}$ ligand is distorted in such a fashion that the 1,2-substituted carbon atoms are in close proximity to W [the $W-C_{ring}$ contact is 2.58(1) Å for both carbons]. Thus, it appears that the W atom is weakly coordinating to the phenyl ring of the bis(amide) ligand.

The chloride ligands of **3** can be substituted with alkyl groups, as shown in eq 3.[12] The dialkyl compounds, **4a**–**d**, were isolated as dark red, air sensitive materials that are very soluble in hydrocarbon solvents. Compounds **4a**–**c** are crystalline solids, while **4d** is an oil. Unlike **3**, **4a**–**d** do not react with σ-donor ligands at room temperature. Despite their formal 14e count, these compounds show no evidence of α-agostic W—H—C interactions and have $^1J_{C-H_\alpha}$ values in the range of 120–130 Hz.



(3)

When compound **4a** was heated to 70 °C in the presence of excess PMe_3, neopentane was eliminated by an α-abstraction reaction, and the five-coordinate alkylidene complex, **5**, was formed in high yield, eq 4.[13] The ^1H NMR spectrum of **5** shows a doublet at 9.62 ppm ($^3J_{P-H}$ = 4 Hz), while the $^{13}C\{^1H\}$ NMR spectrum has a peak at 277.4 ppm. These peaks are assigned to the alkylidene proton and alkylidene carbon atom, respectively. The $^1J_{C-H_\alpha}$ value of 110 Hz is consistent with an α-agostic interaction between the alkylidene proton and the metal center.

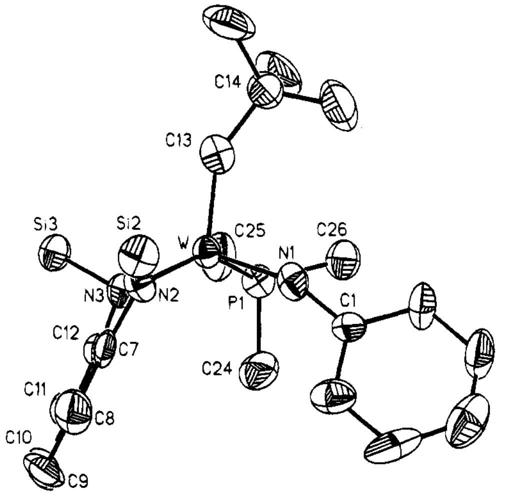
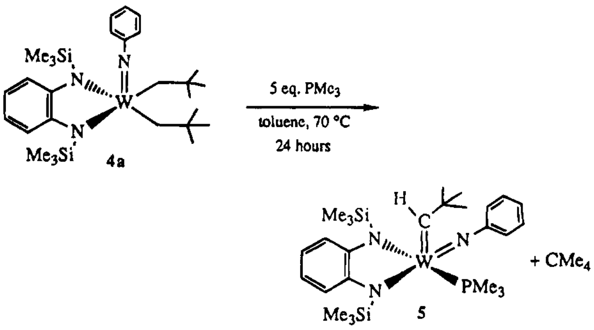


Figure 2. Thermal ellipsoid plot of W(NPh)($CHCMe_3$)-(PMe_3)[$(NSiMe_3)_2C_6H_4$], **5**. The methyl groups have been removed from the silyl groups for clarity. Selected bond distances (Å): W—C(13), 1.884(13); W—N(1), 1.789(9); W—N(2), 2.095(10); W—N(3), 2.067(10); W—P(1), 2.502(4); N(2)—C(7), 1.39(2); N(3)—C(12), 1.40(2). Selected bond angles (°): C(1)—N(1)—W, 160.8(9); C(14)—C(13)—W, 148.4(9); N(2)—W—N(3), 77.8(4).



(4)

Single crystals of **5** that were suitable for X-ray diffraction studies were grown by slowly cooling a pentane solution of **5** to −20 °C. The thermal ellipsoid plot of **5** is shown in Figure 2. The structure of **5** is unique among five-coordinate group 6 alkylidene complexes because it is square pyramidal with the alkylidene carbon in the apical position. The tungsten atom lies 0.61 Å above the square plane defined by the imido nitrogen, the phosphorus atom, and the two amide nitrogens.[14] It is evident that the chelating nature of the [o-$(Me_3SiN)_2C_6H_4]^{2-}$ ligand forces compound **5** to adopt the observed square pyramidal structure rather than a trigonal bipyramidal structure as is observed in *anti*-W(*trans*-CHCH=CHMe)[N-2,6-$C_6H_3(iPr)_2$][OCMe-$(CF_3)_2]_2$(quinuclidene)[15] and W(CHCH=$CHPh_2$)[N-2,6-$C_6H_3(iPr)_2$][OCMe$(CF_3)_2]_2$[P$(OMe)_3$].[16] There is a sig-

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[11] The average deviation of N1, N2, C11, and C12 from the plane is 0.03 Å.

[12] W(NPh)$(CH_2C(CH_3)_3)_2$[$(NSiMe_3)_2C_6H_4$], **4a**: ^1H NMR (C_6D_6) δ 0.54 (s, $SiMe_3$), 1.00 (s, CMe_3), 2.13 (d, J_{H-H} = 10 Hz, $^2J_{W-H}$ = 11 Hz, 2 H, −CH_2CMe₃), 2.29 (d, J_{H-H} = 10 Hz, $^2J_{W-H}$ = 11 Hz, 2 H, −*CH₂*CMe₃); $^{13}C\{^1H\}$ NMR (25 °C in C_6D_6) δ 4.40, 34.8 (−C*Me₃*), 38.32 (−*C*Me₃), 90.8 (J_{C-H} = 123 Hz, −*C*H₂CMe₃).

[13] W(NPh)($CHCMe_3$)(PMe_3)[$(NSiMe_3)_2C_6H_4$], **5**: In a 200-mL glass tube fitted with a Teflon Young's joint, W(NPh)$(CH_2CMe_3)_2$-[$(NSiMe_3)_2C_6H_4$] (1.25 g, 1.87 mmol) was dissolved in 25 mL of toluene. PMe_3 (5 equiv, 0.968 mL, 9.35 mmol) was then added, and the tube was sealed. The reaction was then heated to 70 °C for 24 h. The solution was transferred to a round-bottom schlenk, and solvent was removed under reduced pressure. The brown oil was extracted with pentane, and the volume of the filtrate was concentrated to ca. 15 mL. The solution was cooled to −10 °C to yield 0.83 g of **5** as orange crystals; yield 66.0%. Anal. Calcd for $C_{26}H_{46}N_3PSi_2W$: C, 46.49; H, 6.90; N, 6.26. Found: C, 46.23; H, 6.81; N, 6.05. ^1H NMR (25 °C in C_6D_6): δ 0.38 (s, 9 H, $SiMe_3$), 0.41 (s, 9 H, $SiMe_3$), 0.98 (d, $^2J_{P-H}$ = 10 Hz, 9 H, PMe_3), 1.39 (s, 9 H, CMe_3), 6.68–7.13 (aromatic, 9 H). $^{31}P\{^1H\}$ NMR (25 °C in C_6D_6): δ −2.49 (J_{W-P} = 128 Hz).

[14] The average deviation of N1, N2, N3, and P1 from the plane is 0.03 Å.

nificant lengthening of the W—N_{amide} and W=N bonds in **5** as compared to **3**. The W—N_{amide} bond lengths increase by more that 0.1 Å, while the W=N bond length increases by 0.05 Å in **5**. It is likely that these differences arise from a combination of the increased electron density on the metal center in **5** and the increased steric bulk associated with the neopentylidene and PMe_3 groups in **5** vs the two Cl^- ligands in **3**.

Compound **5** functions as a catalyst for the ROMP of norbornene at room temperature. Norbornene (25 equiv) reacts with **5** over the course of 10 min to give a 90% yield of polynorbornene with M_n = 60 730 and a polydispersity of 1.12.[17] The high molecular weight of the polymer indicates that only a small percentage of **5** initiates as a ROMP catalyst. We expect that loss of PMe_3 from **5** must occur to allow norbornene to coordinate to the metal center so that metathesis can occur. Initial loss of PMe_3 would also explain why only a small fraction of **5** initiates and why **5** must be heated to 70 °C to catalyze the ROMP of cyclooctene or the ADMET oligomerization of 1,9-decadiene.

The reaction of **5** with 5 equiv of PMe_3 and 5 equiv of norbornene was carried out in C_6D_6. The ^1H NMR spectrum of this mixture showed that the reaction proceeded much more slowly, with only 80% of the norbornene being consumed over the course of 1 h. During this time, ca. 35% of **5** was converted to two new alkylidenes that were observed as broad resonances at 9.09 and 9.31 ppm that we believe are *syn* and *anti* isomers of the propagating alkylidene species.[18a] These observations suggest that the addition of PMe_3 to the reaction slows the propagation reaction more than the initiation reaction by inhibiting the loss of PMe_3 from the metal center. These observations are similar to Grubbs's use of PMe_3 to facilitate the living ROMP of cyclobutene to give monodisperse poly-1,4-butadiene.[18b]

We are continuing to explore the use of the $[o\text{-}(R_3SiN)_2C_6H_4]^{2-}$ group as an ancillary ligand for group 6 alkylidene complexes and expect that it will prove useful as an ancillary ligand for other transition metal complexes as well.

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Supplementary Material Available: Full details of the experimental procedures for the synthesis of compounds **1**–**5**, a table of NMR data, and a full description of the X-ray structure determinations of **3** and **5**, including tables of crystal data, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters (26 pages). Ordering information is given on any current masthead page.

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