poor quality of these crystals. All data were collected with $\omega/2\theta$ scan mode. Data were corrected for Lp and for the observed linear decay of the reference reflections. Absorption correction was applied for 15 and 17 by using the DIFABS method;[27] redundant data were merged into a unique data set. The structures were solved with either standard Patterson methods (15, 16), or with direct methods (14, 17) (SHELXS86)[28] and subsequent difference Fourier syntheses. Refinement on F was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carried atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, H atoms were refined with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II–V.

Neutral-atom scattering factors were taken from Cromer and Mann[29] and corrected for anomalous dispersion.[30] All calculations were performed with SHELX76[31] and the EUCLID package (geometrical calculations and illustrations)[32] on a MicroVAX cluster.

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Supplementary Material Available: Tables of anisotropic thermal parameters, torsion angles, all H atom parameters, bond lengths, and bond angles (13 pages); listings of observed and calculated structure factor amplitudes (95 pages). Ordering information is given on any current masthead page.

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Synthesis and Study of Imidoalkyl Complexes of Tungsten(VI): Application of ^{14}N NMR Spectroscopy

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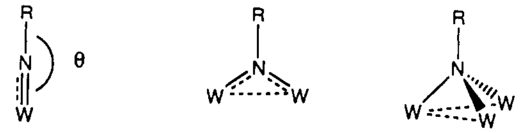
Complexes of the type $W(NR)(CH_2Bu^t)_3X$ have been synthetised by reaction of $WOCl_4$ with RNCO, followed by alkylation with dineopentylmagnesium. The structures of these complexes and their adducts with Lewis acids are proposed. In particular, the use of ^{14}N NMR spectroscopy indicates that the imido–tungsten linkage is linear in both the parent complexes and the adducts, where the binding of the Lewis acid is to the halide and not to the imido ligand.

Introduction

The imido ligand, RN, is proving to be of continuing interest in the chemistry of transition metals in high oxidation states.[1] It possesses properties similar in bonding and reactivity to those of the isoelectronic oxo ligand, but variations in the R group can allow control of the electronic and steric properties that are not available to the oxo group.

The bonding mode of the imido ligand to transition metals is generally one of three types:[1a]



Further, in the monodentate mode, linear coordination ($\theta \approx 180°$) is generally found although bent forms ($\theta \neq 180°$) have also been shown to exist.[2] One difficulty in trying to establish the detailed structures of imido complexes is the lack of a simple physical method to distinguish between these bonding forms. For example, the use of infrared spectroscopy to identify the metal–nitrogen mode and thereby the type of structure has not proved unambiguous.

Some time ago, we were drawn to this problem during our studies on catalysts for the metathesis of olefins. It was observed that oxo–alkyl complexes of W(VI), e.g. $WO(CH_2Bu^t)_3X$ (X = halide), were active for the metathesis of olefins only when strong Lewis acids such as AlX_3 were added.[3] We showed that the initial species formed was the adduct $W(OAlX_3)(CH_2Bu^t)_3X$ where the Lewis acid is bound via the oxo ligand.[4] This research was extended to the synthesis and study of the corresponding imido complexes $W(NR)(CH_2Bu^t)_3X$ (R = Me, Pr^i, Bu^t, 2,6-$(Pr^i)_2C_6H_3$), which we found were active also in the

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methathesis of olefins in the presence of Lewis acids.[3] The synthesis of the analogous phenylimido complexes was also described contemporaneously with our earlier report.[1b] The structure of these complexes has now been studied by ^1H and ^{13}C NMR methods and, in particular, the nature of their interaction with Lewis acids determined by the use of ^{14}N NMR spectroscopy.[5] Although ^{15}N NMR spectroscopy in general would obviously yield more structural information, it suffers from the need to use expensive and not easily accessible ^{15}N products. In contrast, for the structural distinctions required to be made for the complexes described here, ^{14}N NMR data are easily obtained (minutes) without recourse to isotope labeling.

Experimental Section

All manipulations were carried out under nitrogen. The solvents were dried and distilled. $WOCl_4$ was prepared by action of WO_3 and WCl_6 and was sublimed before use. Methyl, isopropyl, and *tert*-butyl isocyanates were sed as received without further purification; $2,6\text{-}(Pr^i)_2C_6H_3NCO$ was prepared following the literature procedure.[6] $(Bu^tCH_2)_2Mg\cdot$(dioxane) was prepared by classical reactions of an alkyl halide on magnesium and then by addition of an excess of dioxane.

NMR spectra were recorded on a Brucker WP 200 spectrometer. The observation frequencies were 200, 87, and 14 MHz, respectively, for ^1H, ^{19}F, and ^{14}N nuclei. Chemical shifts, in ppm, were determined by using the peak of the solvent (C_6D_6) for ^1H and ^{13}C NMR spectroscopy and by using an external reference for ^{14}N and ^{19}F NMR spectroscopy (NH_4^+ and $CFCl_3$, respectively). Infrared spectra were recorded as Nujol mulls (selected peaks only cited). Analyses were carried out by the Service Central d'Analyse (Lyon, France) and the Service de Microanalyse, Institut de Chimie (Strasbourg, France). The mass spectra have been performed on a Thomson THN 208 instrument.

^{14}N NMR Spectra. The samples were prepared in 10-mm NMR tubes; the compounds were dissolved in 10% deuterated solvent and 90% protonated solvent (0.5 mL). Samples 100–200-mg of compound (i.e. ca 0.5–1 $mol\cdot l^{-1}$) were sufficient to obtain a spectrum of good quality in about 1 h, as long as the signal was not too broad. The chemical shifts (δ) were referred to NH_4^+.

The acquisition parameters were as follows: spectrum frequency (SF) = 14.460 MHz; acquisition time (AQ) = 0.406 s; sweep width (SW) = 5000 Hz; pulse width (PW) = 150 ms; relaxation delay (RD) = none; number of scans (NS) = 5000 or more; spectrum reference (SR) -989.014.

Synthesis of $W(NPr^i)Cl_4$ and $W(NPr^i)Cl_4\cdot L$ (L = Et_2O, THF). A mixture of $WOCl_4$ (2 g, 5.8 mmol) and Pr^iNCO (0.75 mg, 8.78 mmol) in heptane (40 mL) was stirred in a sealed flask for 3 days at 110 °C. The solvent was then evaporated under vacuum, and red-brown crystals precipitated. $W(NPr^i)Cl_4$ thus obtained could be used without further purification. This compound could however be recrystallized in CH_2Cl_2, Et_2O, or THF. In the last two cases, orange crystals of $W(NPr^i)CL_4\cdot L$ (L = Et_2O, THF) were collected when a solution of $W(NPr^i)Cl_4$ in those solvents was cooled down to −30°.

Yield for $W(NPr^i)Cl_4$: 80%. ^1H NMR (C_6D_6, 200 MHz): δ 5.87 (hept, 1 H, $NCH\ (CH_3)_2$, $^4J_{HH}$ = 6 Hz), 0.96 (d, 6 H, $NCH(CH_3)_2$). IR (Nujol) (v, cm^{-1}): 1255 (s, WNC), 470–435 (s, WCl): ^{14}N NMR (CD_2Cl_2/C_6D_6, 14 MHz): δ 461.5 (s, line width at half height = 76 Hz). Anal. Found (calc) for $C_3H_7Cl_4NW$ ($W(NPr^i)Cl_4$): C, 9.70 (9.41); H, 1.87 (1.84); N, 3.78 (3.66).

Yield for $W(NPr^i)Cl_4\cdot Et_2O$: 85%. ^1H NMR (C_6D_6, 200 MHz): δ 6.27 (hept, 1 H, $NCH(CH_3)_2$, $^4J_{HH}$ = 6.5 Hz), 4.28 (q, 4 H, $O(CH_2CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 1.16 (d, 6 H, $NCH(CH_3)_2$), 1.03 (t, 6 H, $O(CH_2CH_3)_2$). ^{13}C NMR (C_6D_6, 50 MHz): δ 69.5 (d, $NCH(CH_3)_2$, $^1J_{CH}$ = 104 Hz), 65.6 (t, $O(CH_2CH_3)_2$, $^1J_{CH}$ = 146 Hz, $^2J_{CH}$ = 5 Hz), 22.45 (q, $O(CH_2CH_3)_2$), 12.97 (q, $NCH(CH_3)_2$, $^1J_{CH}$ = 127 Hz). IR (Nujol) (v, cm^{-1}): 1280 (s, WNC), 355 (s, WCl). Mass spectrum (^{182}W), *m/z*: (CI, CH_4) 344 ($M^+ - Et_2O - Cl$); (CI, NH_3) 453 (M^+), 428 ($M + NH_4^+ - Pr^i$), 411 ($M^+ - Pr^i$), 396 ($M + NH_4^+ - Et_2O$).

Synthesis of $W(NMe)Cl_4\cdot L$, $W(NBu^t)Cl_4\cdot L$, and $W(N\text{-}2,6\text{-}(Pr^i)_2C_6H_3)Cl_4\cdot L$. The analogous $W(NMe)Cl_4\cdot L$, $W(NBu^t)Cl_4\cdot L$, and $W(N\text{-}2,6\text{-}(Pr^i)_2C_6H_3)Cl_4\cdot L$ were prepared in the same way, using the starting materials MeNCO, Bu^tNCO, and $(2,6\text{-}Pr^i)_2C_6H_3)NCO$, respectively.

Yield for $W(NMe)Cl_4\cdot THF$: 76%. ^1H NMR (C_6D_6, 200 MHz): δ 5.69 (s, 3 H, $WNCH_3$), $^3J_{WH}$ = 11 Hz), 4.43 (m, 4 H, $(CH_2CH_2)_2O$), 1.27 (m, 4 H, $(CH_2CH_2)_2O$). $^{13}C\{^1H\}$ NMR (C_6D_6, 50 MHz): δ 73.22 ($O(CH_2CH_2)_2$, 53.14 (NCH_3), 26.9 ($O(CH_2CH_2)_2$). IR (Nujol) (v, cm^{-1}): 1315 (w, WNC), 850 (m, THF), 335 (s, WCl). Anal. Found (calc) for $C_5H_{11}ONCl_4W$ ($W(NMe)Cl_4\cdot THF$): C, 13.91 (14.06); H, 2.4 (2.6); N, 3.1 (3.3).

Yield for $W(NMe)Cl_4\cdot Et_2O$: 86%. ^1H NMR (C_6D_6, 200 MHz): δ 5.63 (s, 3 H, $WNCH_3$, $^3J_{WH}$ = 11.3 Hz), 4.28 (q, 4 H, $O(CH_2CH_3)_2$), 1.08 (t, 6 H, $O(CH_2CH_3)_2$).

Yield for $W(N\text{-}2,6\text{-}(Pr^i)_2C_6H_3)Cl_4\cdot THF$: 45%. ^1H NMR (C_6D_6, 200 MHz): δ 7.25 (d, 2 H, $(CH_3)_2CH)C_6H_2H'$, $^1J_{HH}$ = 7.8 Hz), 6.29 (t, 1 H, $((CH_3)_2CH)C_6H_2H'$), 5.03 (hept, 2 H, $((CH_3)_2CH)C_6H_2H'$), 4.48 (m, 4 H, $O(CH_2CH_2)_2$), 1.41 (d, 12 H, $(CH_3)_2CH)C_6H_2H'$, $^1J_{HH}$ = 6.8 Hz), 1.27 (m, 4 H, $O(CH_2CH_2)_2$). ^{13}C NMR (C_6D_6, 50 MHz): δ 156.2 (s), 134.3 (d, $^1J_{CH}$ = 161.2 Hz), 128.5 (d, $((CH_3)_2CH)C_6H_2H'$, $^1J_{CH}$ = 261.4 Hz), 73.5 (t, $O(CH_2CH_2)_2$, $^1J_{CH}$ = 153.7 Hz), 27.8 (d, $((CH_3)_2CH)C_6H_2H'$, $^1J_{CH}$ = 130.8 Hz), 26.3 (q, $((CH_3)_2CH)C_6H_2H'$, $^1J_{CH}$ = 126.4 Hz), 25.4 (t, $O(CH_2CH_2)_2$, $^1J_{CH}$ = 137.3). IR (Nujol) (v, cm^{-1}): 345 (s, WCl). Mass spectrum (^{182}W), *m/z*: (CI, NH_3) 532 ($M^+ + N_2H_7$), 514 ($M^+ + NH_3$), 497 (M^+).

Synthesis of $W(NPr^i)(CH_2Bu^t)_3Cl$. A 1.5-g (5.5 mmol) sample of $(CH_2Bu^t)_2Mg\cdot$(dioxane) dissolved in 50 mL of diethyl ether was added dropwise to a suspension of 1.8 g (4.7 mmol) of $W(NPr^i)Cl_4$ in Et_2O (50 mL). The orange solution that turned to light brown was stirred for $^1/_2$ h. Evaporation of the solvents led to a brown solid that was taken up in 10 mL of pentane. The solution was filtered on Celite and the solvent evaporated again. A brown gum (850 mg) was thus obtained (crude $W(NPr^i)(CH_2Bu^t)_3Cl$, yield 45%). Sublimation (70 °C, 10^{-6} mmHg) yielded 350 mg of a colorless crystalline solid, very soluble in pentane (overall yield: 16%).

$W(NPr^i)(CH_2Bu^t)_3Cl$: ^1H NMR (C_6D_6, 200 MHz) δ 4.29 (hept, 1 H, $NCHMe_2$, $^3J_{HH}$ = 6.6 Hz), 2.21 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 9.7 Hz), 1.29 (d, 6 H, $NCH(CH_3)_2$), 1.18 (s, 27 H, $CH_2C(CH_3)_3$); IR (Nujol) (v, cm^{-1}) 1285 (s, WCN), 1120 (m, CH_2Bu^t), 285 (s, WCl); ^{14}N NMR (C_6H_5Cl/C_6D_6, 14 MHz) δ 335.4 (s, NPr^i, $^1J_{WN}$ = 83 Hz, line width at half-height = 22 Hz). Anal. Found (calc) for $C_{18}H_{40}NClW$ ($W(NPr^i)(CH_2Bu^t)_3Cl$): C, 44.33 (44.14); H, 8.24 (8.23); N, 2.74 (2.86).

Synthesis of $W(NMe)(CH_2Bu^t)_3Cl$, $W(NBu^t)(CH_2Bu^t)_3Cl$, and $W(N\text{-}2,6\text{-}(Pr^i)_2C_6H_3)(CH_2Bu^t)_3Cl$. $W(NMe)(CH_2Bu^t)_3Cl$, $W(N\text{-}2,6\text{-}(Pr^i)_2(C_6H_3)(CH_2Bu^t)_3Cl$, and $W(NBu^t)(CH_2Bu^t)_3Cl$ were prepared in the same manner as $W(NPr^i)(CH_2Bu^t)_3Cl$.

Yield for $W(NMe)(CH_2Bu^t)_3Cl$: 40%. ^1H NMR (C_6D_6, 200 MHz): δ 3.64 (s, 3 H, NCH_3), 2.14 (s, 6 H, $CH_2C(CH_3)_3$, $^2J_{WH}$ = 10.3 Hz), 1.05 (s, 27 H, $CH_2C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 50 MHz): δ 95.5 (CH_2CMe_3), 48.9 (CH_2CMe_3), 36.6 (NCH_3), 33.6 ($CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 14 MHz): δ 307.5 (s, *N*Me, $^1J_{WN}$ = 83 Hz, line width at half-height = 7 Hz). Mass spectrum (^{182}W), *m/z*: (CI, CH_4) 459 (M^+), 424 ($M^+ - Cl$), 388 ($M^+ - CH_2Bu^t$). IR (Nujol) (ν, cm^{-1}) 1310 (m, WNC), 1120 (m, CH_2Bu^t), 270 (s, WCl). Anal. Found (calc) for $C_{16}H_{36}ClNW$: C, 40.33 (41.6); H, 7.43 (7.86); N, 2.63 (3.03).

Yield for $W(N\text{-}2,6\text{-}(Pr^i)_2C_6H_3)(CH_2Bu^t)_3Cl$: 20%. ^1H NMR (C_6D_6, 200 MHz): δ 7.11 (m, 3 H, $(CHMe_2)_2C_6H_3$), 4.09 (hept, 2 H, $(CHMe_2)_2C_6H_3$, $^3J_{HH}$ = 7.2 Hz), 2.53 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 8.8 Hz), 1.29 (d, 12 H, $N\text{-}2,6\text{-}(CH(CH_3)_2)_2C_6H_3$), 1.27 (s, 27 H, $CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 9/1, 14 MHz): δ 310.7 (line width at half-height = 71 Hz).

$W(NBu^t)(CH_2Bu^t)_3Cl$: ^1H NMR (C_6D_6, 200 MHz) δ 2.25 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 10 Hz), 1.36 (s, 9 H, $NC(CH_3)_3$), 1.18 (s, 27 H, $CH_2C(CH_3)_3$); ^{14}N NMR (C_6H_5Cl/C_6D_6, 9/1, 14 MHz) δ 338.8 (line width at half-height = 18 Hz).

Synthesis of $W(NPr^i)(CH_2Bu^t)_3BF_4$. A 300-mg sample of $AgBF_4$ (1.5 mmol) was added as a solid to a solution of 760 mg

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(1.55 mmol) of $W(NPr^i)(CH_2Bu^t)_3Cl$ in 20 mL of benzene. The mixture was stirred for 1 h and filtrated to eliminate AgCl. The solvent was then evaporated under vacuum and the brown solid taken up with 10 mL of *n*-heptane. Colorless cristals (550 mg) were obtained by partial evaporation of the solvent and by cooling down the solution to -30 °C.

Yield for $W(NPr^i)(CH_2Bu^t)_3BF_4$: 65%. ^1H NMR (C_6D_6, 200 MHz): δ 4.28 (hept, 1 H, $NCHMe_2$, $^3J_{HH}$ = 7 Hz), 2.10 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 9.5 Hz), 1.19 (d, 6 H, $NCH(CH_3)_2$)), 1.08 (s, 27 H, $CH_2C(CH_3)_3$)). ^{14}N NMR (C_6H_5Cl/C_6D_6, 9/1, 14 MHz): δ 356 (line width at half-height = 102 Hz). IR (Nujol) (ν, cm^{-1}): 1220 (m, WNC), 1140–1170 (s, BF_4^-). Anal. Found (calc) for $C_{18}H_{40}BF_4NW$: C, 38.42 (39.95); H, 7.53 (7.45).

Synthesis of $W(NPr^i)(CH_2Bu^t)_3F$. A 100-mg sample of NEt_3 (0.99 mmol) was rapidly added to a solution of 240 mg (0.44 mmol) of $W(NPr^i)(CH_2Bu^t)_3BF_4$ dissolved in 10 mL of benzene. The mixture was stirred for 1 h. The solids (identified as Et_3NBF_3 by IR spectroscopy) were then eliminated by filtration on Celite, and the solvent was evaporated under vacuum. The solid obtained was sublimed (60 °C, 10^{-6} mmHg), and 160 mg of colorless crystalline compound was collected.

This complex could also be obtained by exchange of the chlorine of $W(NPr^i)(CH_2Bu^t)_3Cl$, by use of BF_3Et_2O; the boron halides were removed with NEt_3.

Yield for $W(NPr^i)(CH_2Bu^t)_3F$: 75%. ^1H NMR (C_6D_6, 200 MHz): δ 4.39 (hept, 1 H, $NCHMe_2$, $^3J_{HH}$ = 6.5 Hz), 1.91 (d, 6 H, CH_2CMe_3, $^2J_{WH}$ = 10.24 Hz, $^3J_{HF}$ = 10.23 Hz), 1.29 (d, 6 H, $NCH(CH_3)_2$), 1.14 (s, 27 H, $CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 9/1, 14 MHz): δ 336.8 (d, NPr^i, $2J_{FN}$ = 49 Hz, line width at half-height = 16 Hz). Anal. Found (calc) for $C_{18}H_{40}FNW$ ($W(NPr^i)(CH_2Bu^t)_3F$): C, 44.7 (45.67), H, 8.4 (8.52); N, 3.14 (2.96).

Synthesis of $W(NMe)(CH_2Bu^t)_3F$. $W(NMe)(CH_2Bu^t)_3F$ was prepared in the same ways as $W(NPr^i)(CH_2Bu^t)_3F$, using $W(NMe)(CH_2Bu^t)_3Cl$ as starting material.

Yield for $W(NMe)(CH_2Bu^t)_3F$: 85%. ^1H NMR (CD_2Cl_2, 200 MHz): δ 4.26 (s, 3 H, NCH_3), 1.62 (d, 6 H, CH_2CMe_3, $^2J_{WH}$ = 10.5 Hz), 1.05 (s, 27 H, $CH_2C(CH_3)_3$). $^{19}F\{^1H\}$ NMR (C_6D_6, 87 MHz): δ -5.93 (s, WF, $^1J_{WF} \approx$ 50 Hz, $^2J_{NF}$ = 48.9 Hz). ^{14}N NMR (C_6H_5Cl/C_6D_6, 14 MHz): δ 304.7 (d, NMe, $^1J_{WN}$ = 70.9 Hz, $^2J_{FN}$ = 48.9 Hz, line width at half-height = 9 Hz).

Synthesis of $W(NPr^i)(CH_2Bu^t)_3(OCH_2Bu^t)$. A 130-mg (0.27 mmol) sample of $W(NPr^i)(CH_2Bu^t)_3F$ was dissolved in 2 mL of diethyl ether. Then 25 mg (0.27 mmol) of $LiOCH_2C(CH_3)_3$ dissolved in 1 mL of diethyl ether was rapidly added. The mixture was stirred for $^1/_2$ h and was then filtrated on Celite to eliminate LiF, and the solvent was evaporated under vacuum. The 150 mg of colorless solid thus obtained was purified by sublimation (60 °C, 10^{-6} mmHg). A total of 104 mg of crystalline compound was collected.

Yield for ($W(NPr^i)(CH_2Bu^t)_3(OCH_2Bu^t)$): 70%. ^1H NMR (C_6D_6, 200 MHz): δ 4.66 (hept, 1 H, $NCHMe_2$, $^3J_{HH}$ = 6 Hz), 4.22 (s, 2 H, OCH_2CMe_3), 1.68 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 10 Hz), 1.47 (d, 6 H, $NCH(CH_3)_2$), 1.18 (s, 9 H, $OCH_2C(CH_3)_3$), 1.17 (s, 27 H, $CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 9/1, 14 MHz): δ 327.7 (s, NMe, J_{WN} = 61 Hz, line width at half-height = 12.5 Hz). Anal. Found (calc) for $C_{23}H_{51}NOW$ ($W(NPr^i)(CH_2Bu^t)_3(OCH_2Bu^t)$): C, 50.8 (51.02); H, 9.18 (9.49); N, 2.47 (2.59).

Synthesis of $W(NMe)(CH_2Bu^t)_3(OCH_2Bu^t)$. $W(NMe)(CH_2Bu^t)_3(OCH_2Bu^t)$ was prepared in the same way as $W(NPr^i)(CH_2Bu^t)_3(OCH_2Bu^t)$. This colorless compound was purified by sublimation (70 °C, 10^{-6} mmHg).

Yield for $W(NMe)(CH_2Bu^t)_3(OCH_2Bu^t)$: 75%. ^1H NMR (C_6D_6, 200 MHz): δ 4.05 (s, 5 H, NCH_3, OCH_2CMe_3), 1.57 (s, 6 H, CH_2CMe_3, $^2J_{WH}$ = 10 Hz), 1.17 (s, 36 H, $OCH_2C(CH_3)_3$, $CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 14 MHz): δ 295.6 (s, NMe, $^1J_{WN}$ = 65.92 Hz, line width at half-height = 7 Hz).

Synthesis of $W(NMe)(CH_2Bu^t)_3Br$. An excess of pure BBr_3 was added dropwise to a solution of $W(NMe)(CH_2Bu^t)_3(OCH_2Bu^t)$ in diethyl ether to exchange neopentoxide with bromide. The precipitate of $BBr_2(OCH_2Bu^t)$ was removed by filtration and the solvent evaporated. The white product remaining was purified by sublimation (70 °C, 10^{-6} mmHg).

Yield for $W(NMe)(CH_2Bu^t)_3Br$: 56%. ^1H NMR (C_6D_6, 200 MHz): δ 3.53 (s, 3 H, NCH_3), 2.21 (s, 6 H, $CH_2C(CH_3)_3$, $^1J_{WH}$ = 10 Hz), 1.03 (s, 27 H, $CH_2C(CH_3)_3$). ^{14}N NMR (C_6H_5Cl/C_6D_6, 14 MHz): δ 308.8 (s, NMe, $^1J_{WN}$ = 83 Hz, line width at half-height = 8 Hz). IR (Nujol) (ν, cm^{-1}): 1310 (m, WNC), 1115 (m, CH_2Bu^t). Anal. Found (calc) for $C_{16}H_{36}BrNW$: C, 37.85 (37.96); H, 6.99 (7.17); N, 2.96 (2.77); Br, 16.29 (15.78).

Formation of $W(NR)(CH_2Bu^t)_3X{\cdot}AX_3$. The reactions of Lewis acids with the compounds $W(NR)(CH_2Bu^t)_3X$ were studied by ^1H NMR spectroscopy. The imido complex was dissolved in deuterated benzene, AX_3 was added in small portions in the tube, and the spectrum was measured. In all cases no further changes were observed after the addition of 1 equiv of AX_3. The ^{14}N spectrum showed analogous changes, using C_6D_6/C_6H_5Cl as solvent.

Results and Discussion

Synthesis. The imido alkyl complexes, $W(NR)(CH_2Bu^t)_3X$ (1) (R = Me, Pr^i, Bu^t, 2,6-$(Pr^i)_2C_6H_3$; X = F, Cl, Br, $O(CH_2Bu^t)$) were prepared in reasonable yields by the following reactions.

The oxo ligand of $WOCl_4$ was first replaced by the NR group by use of an alkyl or aryl isocyanate:

$$WOCl_4 + RNCO \rightarrow W(NR)Cl_4 + CO_2$$

The use of the reagent $CH_3N(SiMe_3)_2$ could also be used to produce the desired methylimido product but a lower yield was found. Subsequent direct alkylation with 1.5 equiv of $(CH_2Bu^t)_2Mg{\cdot}$(dioxane) yielded the corresponding complexes 1 (X = Cl) in moderate to good yield.

$$2W(NR)Cl_4 + 3(Bu^tCH_2)_2Mg \rightarrow 2W(NR)(CH_2Bu^t)_3Cl + 3MgCl_2$$

The neopentoxo derivatives 1 (X = OCH_2Bu^t) were simply prepared by displacement of chloride in 1 (X = Cl) by treatment with lithium or sodium neopentoxide.

The corresponding bromide complexes of 1 were isolated by reaction of BBr_3 with the neopentoxo analogues. However, the fluoride derivatives were obtained by treatment of 1 (X = Cl) first with $AgBF_4$, forming $(RN)W(CH_2Bu^t)_3(BF_4)$ in good yield, which was then further reacted with NEt_3, causing loss of Et_3NBF_3 and recovery of 1 (X = F).

All complexes of formula 1 were colorless and highly soluble in diethyl ether and pentane. They all were purified by sublimation (60–80 °C, 10^{-6} mmHg). The phenyl analogue has been also synthesized by this method.[1b]

NMR Spectra and Proposed Structure of $W(NR)(CH_2Bu^t)_3X$. The ^1H NMR spectra of all complexes showed two singlets for the protons of the neopentyl ligands (relative intensity 9:2) from the *tert*-butyl and the methylene groups, respectively. The latter resonance showed also satellites resulting from ^{183}W–^1H coupling. Further, the spectra exhibited a singlet (or a heptet when R = Pr^i) at 3.5–4.5 ppm, due to the H of the alkyl group bound to the nitrogen of the imido. No $^2J_{N-H}$ coupling was observed.[7]

No broadening was observed on lowering temperature to -40 °C, indicating that the neopentyls are probably equivalent. A trigonal-bipyramid structure can thus be proposed for $W(NR)(CH_2Bu^t)_3X$, with a terminal alkylimido and the X group (halide or alkoxide) in axial sites, identical with that proposed for the analogous oxo complexes. Such a ligand arrangement is predicted for a pentacoordinate d^0 complex.[8]

Two possible geometries are expected for such a terminal alkylimido group: the bent form when only one $\Pi(\pi \rightarrow \delta)$ interaction is strongly involved in the imido–metal

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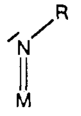
Table I. Pertinent ^{1}H and ^{14}N NMR Data for Imidoalkyl Complexes and Their Lewis Acid Adducts

compd	NC*H*R$_2$^{a} ppm	WC*H*$_2$ CMe$_3$^{a} ppm	*N*R′^{b} ppm	Δν,^{d} Hz	$^1J_{W-N}$, Hz
W(NMe)(CH$_2$CMe$_3$)$_3$-(OCH$_2$CMe$_3$)	4.05	1.57	295.6	7.0	66
W(NMe)(CH$_2$CMe$_3$)$_3$F	3.81	1.85	304.7	9.5	71
W(NMe)(CH$_2$CMe$_3$)$_3$Cl	3.64	2.14	307.5	7.0	83
W(NMe)(CH$_2$CMe$_3$)$_3$Br	3.52	2.17	308.8	8.4	83
W(NMe)CH$_2$CMe$_3$)$_3$Cl/GaCl$_3$	3.60	2.15	343.5^c	9.5	93
W(NMe)(CH$_2$CMe$_3$)$_3$Cl/AlCl$_3$	3.54	2.10	349.8	11.0	105
W(NMe)(CH$_2$CMe$_3$)$_3$Br/AlBr$_3$	3.45	2.10	351.7	9.5	95
W(NPr^i)(CH$_2$CMe$_3$)$_3$-(OCH$_2$CMe$_3$)	4.66	1.68	327.7	12.5	61
W(NPr^i)(CH$_2$CMe$_3$)$_3$Cl	4.29	2.21	335.4	22	83
W(NPr^i)(CH$_2$CMe$_3$)$_3$F	4.39	1.91	336.8	16	65
W(NPr^i)(CH$_2$CMe$_3$)$_3$BF$_4$	4.28	2.10	356.0	102	*e*
W(NPr^i)-(CH$_2$CMe$_3$)$_3$AlCl$_4$	4.19	2.25	392	42	*e*
W(NPr^i)Cl$_4$	5.87		461.5	76	*e*
W(NBu^t)(CH$_2$CMe$_3$)$_3$Cl		2.25	338.8	18	*e*
W(N-2,6-(Pr^i)$_2$C$_6$H$_3$)-(CH$_2$CMe$_3$)$_3$Cl		2.53	310.7	71	*e*

^{a} In C$_6$D$_6$. ^{b} In C$_6$D$_6$/C$_6$H$_5$Cl. ^{c} In C$_5$H$_{12}$/C$_6$H$_5$Cl. ^{d} Width at mid-height. ^{e} Not measurable, signal too broad.

bonding or the linear form when two Π bonds are created between the nitrogen and the metal.



bent form

linear form

Since tungsten in these complexes is formally of configuration d^0, we might anticipate the presence of the latter structure.

Indeed, the ^{1}H NMR spectra of our compounds did not show noticeable peak broadening on the NC*H*R$_2$ resonance (R = H or Me), suggesting a weak quadrupolar effect and thus a linear type geometry.[9] In order to confirm this interpretation we studied these compounds by ^{14}N NMR spectroscopy. Normally, sharp spectra would only be obtained if the electronic charge distribution about the ^{14}N nucleus is relatively symmetrical. The bent form (by analogy with imines) would be expected to give a broad resonance whereas linear bonding should present a sharp resonance (cf. R—N≡C).[9] The ^{14}N NMR spectra of the complexes 1 were readily obtained and the data are collected in Table I, along with some ^{1}H NMR data and coupling constant measurements. Sharp peaks generally of line widths at half-height of Δν = 7–20 Hz were obtained in most cases, which can be compared with the ^{14}N NMR spectra of organic molecules generally showing a Δν of 100–2000 Hz[9]. ^{14}N–^{183}W (^{183}W $S = {}^1/_2$, natural abundance 14.4%) coupling could also be observed, when the signal was not too broad (Δν ≤ 22 Hz).

This can be illustrated by the ^{14}N spectrum obtained for W(NMe)(CH$_2$Bu^t)$_3$F (Figure 1), where the ^{14}N resonance is split into a doublet by ^{19}F coupling ($^2J_{^{14}N-^{19}F}$ = 49 Hz), with weak, but reproduceable, satellites resulting from $^1J_{^{14}N-^{183}W}$ coupling also present in the spectrum.

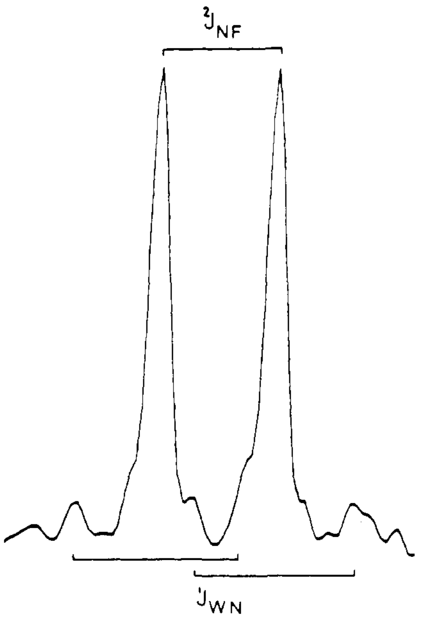
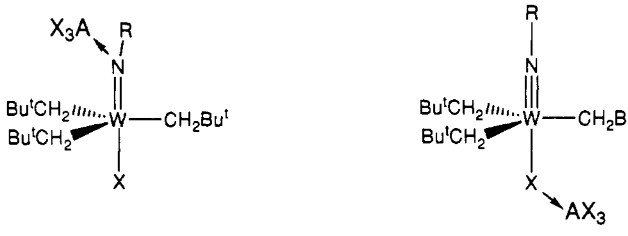


Figure 1. ^{14}N NMR spectrum of W(NMe)(CH$_2$Bu^t)$_3$F.



2a 2b

Figure 2. Possible interactions of 1 with a Lewis acid.

The presence of the ^{14}N–^{19}F coupling was confirmed by the ^{19}F NMR spectrum, which also shows ^{183}W–^{19}F satellites (see Experimental Section).

In the case of the arylimido complex, 2, the ^{14}N resonance is significantly enlarged (width at half-height ≈ 70 Hz) and ^{14}N–^{183}W coupling was not observed. Such broadening of ^{14}N resonances by an attached phenyl group is not without precedent.[9] Some broadening is also observed when the methyl group of the imido is replaced by an isopropyl or a *tert*-butyl.

The complexes of the type W(NMe)(CH$_2$Bu^t)$_3$X show ^{14}N chemical shifts in the range δ 295–340 ppm, the shifts increasing in the order NpO < F ≈ Cl < Br. This sequence is not related to the electronegativity of the X ligand and appears to be best interpreted as largely following the order of decreasing Π-donor ability of the trans ligand X. As the Π-donation from X to W decreases, the imido ligand Π-interaction will increase and the effective positive charge on N will thereby augment, shifting the resonance downfield. Clearly such an interpretation is oversimplified, as shown by the change in relative order of the F and Cl ligands in changing NMe with NPr^i. Overall, however, in these complexes we confirm that the imido to tungsten interaction probably involves a linear arrangement, as predicted.

Interaction of 1 with Lewis Acids. As we have previously found for the corresponding oxo complexes, addition of Lewis acids AlX$_3$ to 1 in chlorobenzene solutions creates active catalysts for the metathesis of the olefins. We suggested by analogy with the oxo complexes, that the Lewis acid interacted with the imido group to form com-

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plex **2a**, which initiated reductive α-elimination of neopentane and thus carbene formation. However, with the subsequent isolation and characterization by X-ray methods of the catalysts $W(CHR)(OR)_2X(\mu^2\text{-}AX_4)$, where binding of the Lewis acid via a halide ligand is found,[10] the structure **2b** for the adduct seemed also feasible. Indeed, whereas binding of the Lewis acid to a terminal oxo group is possible via the nonbonding electrons on oxygen, thereby leaving the two ($\pi \rightarrow \delta$) Π-bonds intact, the corresponding interaction with the metal–imido group will necessarily cause loss of one such Π-bond (see Figure 2). Further, given the additional steric interaction in the formation of **2a**, it seemed that **2b** might be the more stable isomer. ^{14}N NMR spectroscopy is particularly suited to solve this problem, as we would anticipate **2a** to show a broad resonance, in contrast to **2b** where a narrow absorption might be expected.

When the Lewis acid (AlX_3 (X = Cl, Br), $GaBr_3$) is added by small portions to the complex in deuterated benzene, a shift of all the peaks is observed in the ^1H NMR spectra. This phenomenon occurs until 1 equiv of Lewis acid/$W(NR)(CH_2Bu^t)_3X$ has been added; the addition of more AX_3 does not modify the chemical shifts, showing that a strong adduct (in a 1:1 ratio) is formed in solution. The ^1H NMR spectra of the adducts are similar to those of the free complexes. The peaks, most notably those of the α-protons of the imido group, remain sharp, again no quadrupolar broadening by the nitrogen being observed. The resonances corresponding to the protons of the neopentyl and the imido groups were both displaced upfield by about 0.05 ppm. The former shift is considerably less than for the oxo analogues (ca. 1 ppm),[3] where also, in contrast, the shift is downfield, leading us to suspect a structural difference between the oxo and imido adducts.

The ^{14}N NMR spectra showed a downfield shift of about 45–55 ppm on Lewis acid adduct formation. Importantly, the resonance is still sharp (9.5–40 Hz) and the $^1J_{^{183}W-^{14}N}$ coupling is still observed in the case of the methyl-imido and increases by 10–20%. Both these latter observations indicate that the adduct has the structure **2b**, since coordination to the halide should (a) leave the electric field gradient about the nitrogen nucleus essentially unchanged yielding a narrow resonance and (b) cause an increase in the $^2J_{^{183}W-^{14}N}$ coupling constant as a result of the tighter binding of the imido group to tungsten.

We further note that the large downfield shift of the ^{14}N resonance when the Lewis acid binds to the trans X ligand is indicative of a large positive charge development on N. This no double results from both the reduction of Π-bonding by the X group and an increase in ionic contribution ($W^{\delta+}\text{-}XAX_3^{\delta-}$) to the σ-bonding, resulting from the strongly electronegativity nature of the AX_4^- ligand. Interestingly, this would imply that, in complexes **1**, the contribution of Π-back-bonding to the metal from the X ligand must be relatively large to give the chemical shift trend found, which is almost the reverse of that expected from electronegativity considerations.

Conclusion

The complexes of the type $(RN)W(CH_2Bu^t)_3X$ (**1**) would seem to possess a linear tungsten–imido linkage as would be expected for a d^0 metal complex. However ^{14}N studies show that for the catalyst combinations of **1** with Lewis acids, the binding of the Lewis acid is to the trans X ligand and *not* to the imido ligand, in contrast to that found for the analogous oxo complexes. Further, the ^{14}N NMR shift data indicate that the Π-bonding contribution of the X–W interaction must be important and follows the order RO $>$ F $\approx$ Cl $>$ Br $>$ I.

Acknowledgment. We thank the CNRS for financial support.

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