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# Synthesis and reactivity of the imidotungsten methyl cation $[W(N_2N_{py})(NPh)Me]^+$: $CO_2$ adds to the W=NPh bond and does not insert into the W–Me bond†

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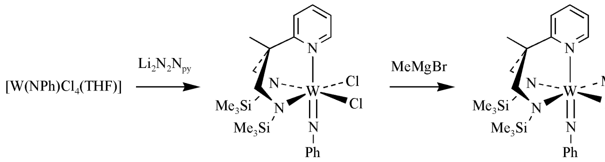
**The imidotungsten dimethyl compound $[W(N_2N_{py})(NPh)Me_2]$ 2 reacts with $BAr^F_3$ to form the cationic complex $[W(N_2N_{py})(NPh)Me]^+$ $3^+$ [anion = $[MeBAr^F_3]^-$; $Ar^F$ = $C_6F_5$; $N_2N_{py}$ = $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$] which undergoes methyl group exchange with added 2, $[Cp_2ZrMe_2]$ or $ZnMe_2$; treatment of cation $3^+$ with $CO_2$ or isocyanates leads to cycloaddition reactions at the W=NPh bond and not insertion into the W–Me bond, despite the latter product being the most thermodynamically favourable according to DFT calculations.**

Broadly speaking, the molecular reactions of transition metal imido complexes $[M(NR)_n(L)_m]$ (R = alkyl or aryl; $(L)_m$ = supporting ligand or ligand set) fall into two categories: (*i*) those in which the M=NR linkage is the reactive site undergoing transformations such as activation and coupling of saturated or unsaturated organic substrates, and (*ii*) those where the imido group(s) act as 'ancillary' or 'spectator' ligands with the transformation(s) being studied occuring at some other part of the molecule.[1] One of the best known examples of this latter category from Group 6 are the olefin metathesis catalysts $[M(NAr)(CHR)(OR')_2]$ (M = Mo or W, Ar = 2,6-$C_6H_3{}^iPr_2$, R′ = bulky alkyl or aryl group) which undergo cycloaddition reactions at the M=CHR alkylidene group.[1d,e] Another example from Group 6 is provided by Gibson's bis(imido)chromium(VI) compounds $[Cr(NR')_2R_2]$ (R′ = ${}^tBu$ or aryl, R = Me or $CH_2Ph$) which provide very active and long-lived ethylene polymerisation catalysts.[2] At first sight these appear to be relatively simple cases where an active cationic species of the form $[Cr(NR')_2R]^+$ (R = growing polymer chain) would be anticipated, with propagation straightforwardly involving the incoming ethylene weakly coordinating to the $d^0$ metal and undergoing migratory insertion into the Cr–R bond. However, very recent calculations by Jensen and Børve[3] have cast doubt on this picture. For chemically realistic model systems of $[Cr(NR')_2R]^+$ it appears that ethylene cycloaddition to the Cr=NR′ bond can compete with insertion into the Cr–R bond, in turn leading (after further modification) to a reduced Cr(IV) species which may in fact be the resting state for this catalyst system. In the light of these results, and their serious implications for the design and mechanistic interpretation of imido-base reagents and catalysts, it is clearly important to harvest more information concerning the relative reactivity aptitudes of competing metal–alkyl and metal–imide functionalities towards unsaturated substrates. Here we outline the synthesis and reactions of a cationic imidotungsten(VI) methyl complex with heterocumulenes and show how insertion of these substrates into a tungsten–alkyl bond is kinetically disfavoured compared to cycloaddition at the tungsten–imide bond.

As part of an ongoing program in early transition metal imido chemistry[4a] using the diamide-donor ligand[4b,c] $MeC(2\text{-}C_5H_4N)(CH_2NSiMe_3)_2$ (abbreviated as $N_2N_{py}$) we prepared the dimethyl complex $[W(N_2N_{py})(NPh)Me_2]$ **2** according to eqn. (1) in 35% yield from the dichloride **1**.† The di-$^{13}CH_3$ and di-$CD_3$ isotopomers of **2** were similarly prepared and have been used in parallel with **2** throughout this work to support the proposed structures and reactions. The X-ray structure of **2** is shown in Fig. 1 and establishes the connectivity and other geometrical features.† Reaction of **2** with $BAr^F_3$ ($Ar^F$ = $C_6F_5$) in $CD_2Cl_2$ formed the five-coordinate cation $[W(N_2N_{py})(NPh)Me]^+$ $\mathbf{3}^+$ and the anion $[MeBAr^F_3]^-$ which, according to the $^1H$ and $^{19}F$ NMR spectra, is non-coordinating in this solvent.[5] Cation $\mathbf{3}^+$ decomposes only fairly slowly (half-life *ca.* 2 h) at room temperature in $CH_2Cl_2$ or $CD_2Cl_2$ thereby allowing ample opportunity to explore its reactivity. Although too reactive to be obtained in the solid state, $\mathbf{3}^+$ can be stabilised and isolated as the acetonitrile adduct $[W(N_2N_{py})(NPh)(MeCN)Me]^+$ $\mathbf{4}^+$ (anion = $[MeBAr^F_3]^-$). To the best of our knowledge these cationic imido alkyl complexes are only the second such examples from Group 6 to be reported, the other



**1** **2** (1)

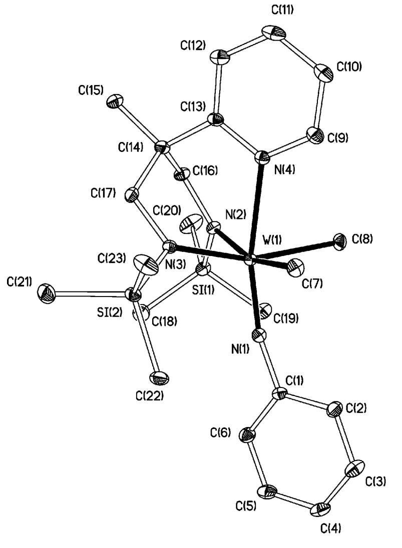


**Fig. 1** Displacement ellipsoid plot (20%) of $[W(N_2N_{py})(NPh)Me_2]$ **2** with H atoms omitted for clarity. Selected distances (Å) and angles (°): W(1)–N(1) 1.745(2), W(1)–N(2) 1.997(2), W(1)–N(3) 2.042(2), W(1)–N(4) 2.336(2), W(1)–C(7) 2.250(2), W(1)–C(8) 2.228(2), W(1)–N(1)–C(1) 164.8(2).

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† Electronic supplementary information (ESI) available: crystal data for **2**, DFT/computational notes, supporting characterising data and selected experimental details for the new compounds. See http://www.rsc.org/suppdata/cc/b2/b208327b/

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being the chromium bis(imido) species $[Cr(N^tBu)_2(CH_2Ph)]^+$ alluded to above and characterised *in situ*.[2] Apart from its reactivity with ethylene, no other reactions of this species were reported (other than the formation of Lewis base adducts).

Treatment of **2** with half of an equivalent of $BAr^F_3$ gives solutions containing the binuclear methyl-bridged cation $[W_2(N_2N_{py})_2(NPh)_2Me_2(\mu\text{-}Me)]^+$ **5**$^+$ which can also be formed by treating methyl cation **3**$^+$ with one equivalent of dimethyl **2**. Labelling studies (treatment of either $[W(N_2N_{py})(NPh)(^{13}CH_3)_2]$ or $[W(N_2N_{py})(NPh)(CD_3)_2]$ with one equivalent of $[W(N_2N_{py})(NPh)Me][MeBAr^F_3]$ **3**) show that the methyl groups in **5**$^+$ all scramble (but not with the methyl of the anion $[MeBAr^F_3]^-$). Treatment of **5**$^+$ with an equivalent of $BAr^F_3$ gave complete conversion to $[W(N_2N_{py})(NPh)Me]^+$. The formation of a bridging methyl cation like **5**$^+$ is precedented for main group, actinide and early transition metals.[6] Interestingly, $[W(N_2N_{py})(NPh)Me]^+$ also undergoes intermolecular methyl group exchange with $ZnMe_2$ on the NMR timescale (confirmed by a spin saturation transfer NMR experiment), and also slowly with $[Cp_2ZrMe_2]$ (as established by deuterium labelling experiments with $[W(N_2N_{py})(NPh)CD_3]^+$ or $[Cp_2Zr(CD_3)_2]$) presumably through methyl bridged intermediates analogous to **5**$^+$. In these regards, therefore, the imidotungsten methyl species **3**$^+$ has ‘normal’ alkyl cation behaviour and hence was a good candidate to compare its reactivity towards substrates that might react at either the W–Me or the W=NPh bond.

Unfortunately $[W(N_2N_{py})(NPh)Me]^+$ **3**$^+$ does not react at all with ethylene so we could not make comparisons with the computational predictions concerning the $[Cr(NR')_2R]^+$ systems. However, insertion reactions of tungsten alkyl compounds with $CO_2$ (to form O-bound acetate derivatives) have been carefully studied in detail;[7] moreover, we ourselves[8*a*,*b*] have recently been exploring the still quite rare $CO_2$ activation reactions of transition metal imides,[8] which have not before been identified in Group 6 imido chemistry at all. Reaction of **3**$^+$ with $CO_2$ (Scheme 1) proceeds rapidly and quantitatively at room temperature to form the N,O-bound carbamate product of imide cycloaddition $[W(N_2N_{py})\{N(Ph)C(O)O\}Me]^+$ **6**$^+$ and *not* the alternative insertion product $[W(N_2N_{py})(NPh)(O_2Me)]^+$ **7**$^+$ (Scheme 1) or one of its isomers. Support for formulating the $CO_2$ reaction product as **6**$^+$ and not **7**$^+$ comes from $^{13}C$ labelling studies (of both the methyl group in **3**$^+$ and in the $CO_2$): no $^{13}CH_3$–$^{13}CO_2$ coupling is observed in doubly-labelled **6**$^+$, and the magnitude of the $^{183}W$–Me coupling constant ($^1J_{W-Me}$ = 92 Hz) is comparable to those in **2**, **3**$^+$ and **4**$^+$. Reaction of **3**$^+$ with phenyl isocyanate gives an analogous N,N′-bound ureate, imide cycloaddition product $[W(N_2N_{py})\{N(Ph)C(O)N(Ph)\}Me]^+$ **8**$^+$ and, again, *not* insertion into the W–Me bond. Hydrolysis of **8**$^+$ afforded the expected derivative diphenylurea as one of the products thus confirming the ureate ligand’s presence in **8**$^+$.

The reactions of $[W(N_2N_{py})(NPh)Me]^+$ **3**$^+$ described above, which give exclusively products of cycloaddition at the W=NPh bond, appear to be governed by *kinetic* factors. Thus, DFT (B3PW91) calculations† of model systems for $[W(N_2N_{py})\{N(Ph)C(O)O\}Me]^+$ **6**$^+$ and $[W(N_2N_{py})(NPh)(O_2Me)]^+$ **7**$^+$ have shown that the W–C *insertion* product **7**$^+$ is in fact actually 50.6 kcal mol$^{-1}$ *more stable* than the *observed* W=N *cycloaddition* product **6**$^+$. Detailed experimental and computational studies of the reactions and products of $[W(N_2N_{py})(NPh)Me]^+$ **3**$^+$ and related compounds with a number of unsaturated organic substrates are currently underway to identify the underlying mechanistic and other factors governing the reactions of imido alkyl complexes. The question of at which point *ancillary* imido ligands become *reactive* ligands in chemical transformations will have clear implications for the use of imido-based species in catalytic and stoichiometric chemistry.

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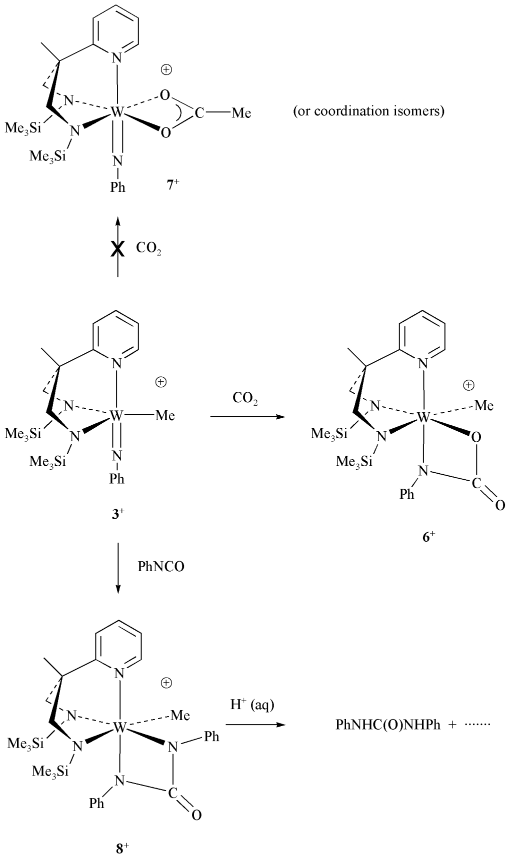

**Scheme 1** Synthesis and reactions of $[W(N_2N_{py})(NPh)Me]^+$ **3**$^+$ (anion = $[MeBAr^F_3]^-$).

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