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# $d^2$ Complexes of tungsten containing *p*-toluonitrile as a four- or two-electron donor and oxidative addition giving the two-electron donor acylimido ligand $NCOC_6H_4Me$-4†

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Reaction of benzonitrile with $WCl_6$ in the presence of $CCl_2CCl_2$ gave the complex $[\{WCl_4(NCPh)\}_x]$ of undetermined structure which does not show equivalent chemistry to the $d^0$ complexes $[\{WCl_4(PhC_2Ph)\}_2]$ and $[\{WCl_4(NPh)\}_2]$. The complex $[WCl_2(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_3]$ **1** can be prepared by reduction of $[WCl_4(PMe_3)_3]$ with 2 equivalents of Na/Hg amalgam in the presence of *p*-toluonitrile. The nitrile carbon in the $^{13}C\text{-}\{^1H\}$ NMR spectrum appears at δ 232.2 consistent with a four-electron donor nitrile ligand. Reaction of $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ with purified *p*-toluonitrile in refluxing toluene or reduction of $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_2]$ in benzene with 1 equivalent of Na/Hg amalgam in the presence of *p*-toluonitrile led to $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_2]$ **2** as shown by $^1H$, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The position of the nitrile carbon in the $^{13}C\text{-}\{^1H\}$ NMR spectrum (δ 178.9) is consistent with a two-electron donor nitrile ligand. Reaction of $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ with unpurified *p*-toluonitrile gave $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)(OPMe_3)(PMe_3)]$ **3** in addition to **2**. A crystal structure determination showed *cis* orientated imido and acylimido ligands [W−N 1.769(5) and 1.823(6) Å, W−N−C 174.5(5) and 158.9(5)°], *cis*-chloro ligands and a *cis* orientation of the $PMe_3$ and $OPMe_3$ ligands. The bond lengths and angles about the NCOPh function are not significantly different to those of a variety of uncomplexed organic amide groups. Hartree–Fock and density-functional calculations performed on the model complex $[WCl_2(NMe)(NCOH)(OPH_3)(PH_3)]$ **4** showed structural parameters in good agreement with those of **3** when the phenyl groups were removed. An NBO (natural bond orbital) analysis of the W−NMe bond generated one σ and two π bonds between nitrogen s and p atomic orbitals (AOs) and tungsten d AOs. The nitrogen of the NCOH ligand binds to tungsten *via* one σ and one π bond. In contrast to the NMe ligand, the NBO analysis located a nitrogen 'lone pair' orbital on the NCOH ligand which overlaps somewhat with the C−O π orbitals (11% for carbon, 5% for oxygen) and with tungsten (8%). The structural and theoretical studies indicate the NMe ligand nitrogen atom dominates the π donation.

The concept that alkyne ligands are capable of stabilising high oxidation states of early transition metal complexes on the basis of strong π donation from the ligand to the metal as found in organoimido complexes has gained credence over time.[1] Our work with tungsten–alkyne complexes has demonstrated that the four-electron donor diphenylacetylene complexes $[\{WCl_4(PhC_2Ph)\}_2]$, $[WCl_3(PhC_2Ph)(PR_3)_2]$ and $[WCl_2(PhC_2Ph)(PR_3)_3]$ ($PR_3 = PMe_3$ or $PMe_2Ph$) should be regarded as $d^0$, $d^1$ and $d^2$ systems respectively,[2] while the two-electron donor diphenylacetylene complexes $[WCl_2(NR)(PhC_2Ph)(PMe_3)_2]$ (R = Ph[3] or $C_6H_3Pr^i_2$-2,6[4]) are $d^2$ systems. The emergence of a limited number of two- and four-electron donor $\eta^2$-organonitrile complexes,[5–7] led us to consider that this tungsten–alkyne chemistry might be duplicated by organonitriles. We report here the results of these studies which include an unprecedented reaction of an organonitrile leading to an acylimido ligand.

## Results and Discussion

### Synthetic studies

The preparation of $[\{WCl_4(PhC_2Ph)\}_2]$ involves refluxing $WCl_6$ and $PhC_2Ph$ in $CH_2Cl_2$ in the presence of tetrachloroethylene.[8] When $WCl_6$ and 1 equivalent of benzonitrile were treated in this way a deep red solution was obtained which gave rise to a brown solid which analysed near to the formulation $[\{WCl_4(NCPh)\}_x]$ but the $^1H$ NMR spectrum exhibited very broad resonances indicating the complex is not a $d^0$ system. In addition the complex did not show the reductive chemistry of $[\{WCl_4(PhC_2Ph)\}_2]$ whereby the $d^1$ and $d^2$ complexes $[WCl_3(PhC_2Ph)(PMe_3)_2]$ and $[WCl_2(PhC_2Ph)(PMe_3)_3]$ are easily prepared,[2] forming ill-defined products instead when these reactions were attempted. Efforts further to characterise $[\{WCl_4(NCPh)\}_x]$ have been hampered by its extreme air sensitivity. We have not yet been able to grow crystals, obtain reliable ESR spectra or magnetic moment data although the latter clearly shows paramagnetism as indicated by the $^1H$ NMR spectrum.

In exploring other routes to four-electron donor $\eta^2$-organonitrile complexes we attempted to form $d^1$ complexes by methods involving an oxidative addition of the organonitrile to lower-valent complexes. However such reactions as the reduction of $[WCl_4(PMe_3)_2]$ with 1 equivalent of Na/Hg amalgam in the presence of *p*-toluonitrile or reaction of this potential ligand with $[WCl_3(PMe_3)_3]$ did not give rise to the anticipated complex $[WCl_3(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_2]$. Subsequent reduction of $[WCl_4(PMe_3)_3]$ with Na/Hg amalgam in the presence of *p*-toluonitrile gave $[WCl_2(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_3]$ **1** as a green solid [equation (1)]. A similar reduction has been used to obtain the green complex $[WCl_2(\eta^2\text{-}NCMe)(PMe_3)_3]$.[6]

$$[WCl_4(PMe_3)_3] + NCC_6H_4Me\text{-}4 \xrightarrow[\text{tetrahydrofuran}]{\text{2Na/Hg}} \underset{\textbf{1}}{[WCl_2(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_3]} \quad (1)$$

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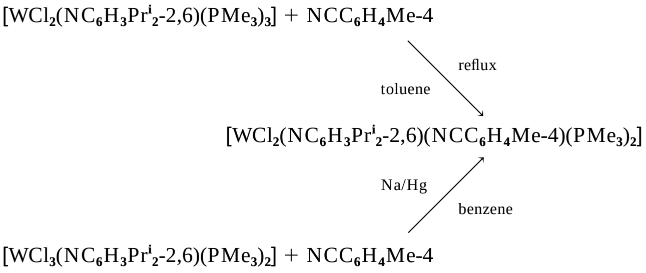
† Dedicated to the memory of Professor Sir Geoffrey Wilkinson FRS.

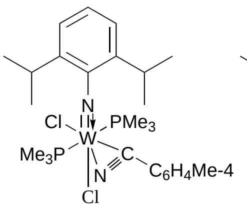


**Scheme 1**

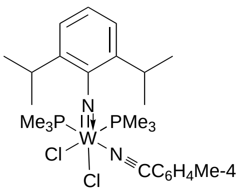
Complex **1** showed a doublet and a triplet in the $^1H$ and $^{13}C\text{-}\{^1H\}$ NMR spectra indicating a meridional disposition of the three phosphine ligands and there was a single set of resonances for the relevant proton or carbons of the nitrile ligand. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the nitrile carbon appeared at $\delta$ 232.2 as a multiplet arising from coupling to two different types of phosphines. These NMR features point to an $\eta^2$-nitrile, *mer*-phosphine-*cis*-dichloro structure based on the similarities of these spectra to the crystallographically determined complex $[WCl_2(\eta^2\text{-}NCMe)(PMe_3)_3]$ in which the nitrile ligand acts as a four-electron donor.[6] The position of the nitrile carbon at $\delta$ 232.2 in the $^{13}C\text{-}\{^1H\}$ NMR spectrum for **1** is similar to that found for the acetylenic carbons in $[WCl_2(PhC_2Ph)(PMe_3)_3]$ for which spectroscopic and structural studies as well as theoretical calculations suggest a $d^2$ configuration.[2] An X-ray photoelectron (XPS) spectrum of **1** shows a $W(4f_{\frac{7}{2}})$ binding energy of 32.9 eV (1 eV $\approx 1.60 \times 10^{-19}$ J) which is of similar magnitude to that found for $[WCl_2(PhC_2Ph)(PMe_3)_3]$ and $[WCl_2(NPh)(PMe_3)_3]$ (32.7 and 32.5 eV respectively[2]) suggesting the nitrile analogue **1** may also have a $d^2$ configuration.

Having obtained a four-electron donor $\eta^2$-organonitrile complex it was of interest to prepare a two-electron donor equivalent. We have reported that tungsten(IV) organoimido complexes $[WCl_2(NR)(\eta^2\text{-}L)(PMe_3)_2]$ (R = Ph, $CHMe_2$ or $C_6H_3\text{-}Pr^i_2\text{-}2,6$; L = olefins, alkynes)[3,4,9] may be conveniently prepared either by exchanging a phosphine ligand in the complexes $[WCl_2(NR)(PMe_3)_3]$ by L or by reducing the tungsten(V) complexes $[WCl_3(NR)(PMe_3)_2]$ in the presence of L. In a continuation of this work these methods were used to determine if organonitriles would form similar side-bound complexes. When $[WCl_2(NPh)(PMe_3)_3]$[10] was refluxed with a variety of alkyl or aromatic nitriles in organic solvents very little reaction took place while extended reaction periods (*ca.* several days) caused decomposition of the tungsten complex in varying amounts. However, when $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$[4] was refluxed in toluene for several hours with freshly dried and distilled *p*-toluonitrile, $PMe_3$ was given off and a complex analysing as $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NCC_6H_4Me\text{-}4)(PMe_3)_2]$ was obtained. The same complex was formed when $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_2]$ was reduced with 1 equivalent of Na/Hg amalgam in the presence of *p*-toluonitrile (Scheme 1).

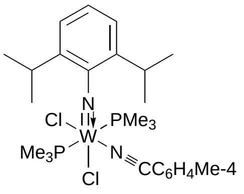
Attempts to crystallise the product from a variety of solvents led to decomposition but characterisation as the complex $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_2]$ **2** was made by NMR spectroscopy. The $^1H$ and $^{13}C\text{-}\{^1H\}$ NMR spectra showed two doublets for the two $PMe_3$ ligands suggesting a *cis* orientation, but the $^{31}P\text{-}\{^1H\}$ NMR spectrum showed an AB quartet with $^2J(PP)$ of 183.3 Hz consistent with *trans* phosphines in an asymmetric environment.[2–4] Asymmetry can only arise in this molecule if an $\eta^2$-bound nitrile ligand is present (structure **I**) and not if *cis* or *trans* phosphines are present with an $\eta^1$-bound nitrile (stuctures **II** and **III**). Further evidence for this type of bonding comes from the $^{31}P\text{-}\{^1H\}$ NMR spectrum where two P–W coupling constants were observed [$^1J(PW)$ 253.1 and 242.5 Hz] which are consistent with small differences in the two W–P bond lengths arising from proximity of the asymmetric $\eta^2$-bound ligand. This type of relationship has been determined by NMR spectroscopy and X-ray crystallography for $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(HC_2Ph)(PMe_3)_2]$.[4]



**I**



**II**



**III**

Other features of the NMR spectra also reflect the side-bound nature of the nitrile. In the $^1H$ NMR spectrum the imido ligand isopropyl group C–H resonances are widely separated at $\delta$ 2.52 and 4.41 with one set of methyl groups appearing as a broadened doublet and the other set as two doublets. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum there are two isopropyl C–H resonances and four methyl group resonances. The NMR spectra thus indicate that the four methyl groups are diastereotopic which is also a spectral feature of $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(HC_2Ph)(PMe_3)_2]$.[4] The nitrile carbon resonance for **2** appeared as a doublet of doublets centred at $\delta$ 178.9 which is in the region found for other two-electron donor $\eta^2$-organonitrile complexes,[5] and the imido ligand *ipso* carbon appeared at $\delta$ 148.5 which is similar to those for other 2,6-diisopropylphenylimido complexes in a $d^2$ electron configuration.[4]

When $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ was refluxed in toluene with an unpurified sample of *p*-toluonitrile NMR spectroscopy indicated that in addition to complex **2** the reaction gave reproducibly a small quantity of another complex. A toluene solution of the mixture layered with light petroleum gave a yellow crystalline solid for which analytical data suggested the formula $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NCC_6H_4Me\text{-}4)(OPMe_3)_2]$. However the NMR spectra were not consistent with this formulation with the $^1H$ and $^{13}C\text{-}\{^1H\}$ showing two doublets for the phosphorus ligands and two singlets in the $^{31}P\text{-}\{^1H\}$ NMR while the *ipso*-carbon resonances of the two aromatic rings occurred at $\delta$ 140.4 and 142.1. This region of the spectrum is not that found for the C≡N carbon of four- or two-electron donor nitrile ligands or for $\eta^1$-nitrile complexes where the resonance of the nitrile carbon appears close to that of the free ligand.[11] A crystal structure determination showed alternatively that the product was the bis(imido) complex $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)(OPMe_3)(PMe_3)]$ **3**.

The structure (Fig. 1) shows a distorted octahedral array with a *cis* orientation of the nitrogen ligands. The $Me_3PO$ ligand lies *trans* to the 2,6-diisopropylphenylimido ligand while a chloro ligand lies *trans* to the other nitrogen function. The W–N(2) bond length [1.769(5) Å] and W–N(2)–C(21) bond angle [174.5(5)°] (Table 1) are consistent with a 'linear' four-electron donor (1$\sigma$, 2$\pi$ interaction) 2,6-diisopropylphenylimido ligand.[4] The W–N(1) bond length [1.823(6) Å] is only slightly shorter than that of the two-electron donor (1$\sigma$, 1$\pi$ interaction) *p*-tolylimido ligand in $[\{WCl_2(NC_6H_4Me\text{-}4)(NBu^t)(NH_2\text{-}Bu^t)\}_2]\cdot1.6CHCl_3$[12] [W–N bond length 1.890(9) Å] where the lone pair donates to the other tungsten atom of the dimer. This suggests that the acylimido ligand in **3** is also a 1$\sigma$, 1$\pi$ donor with a free lone pair which contrasts with other bis(organoimide) complexes of tungsten(VI) where the six electrons are spread over both ligands.[13] In molybdenum chemistry

**Table 1** Selected bond lengths (Å) and angles (°) for complex **3**

| | | | |
|---|---|---|---|
| W–N(1) | 1.823(6) | W–P(2) | 2.523(2) |
| W–N(2) | 1.769(5) | N(1)–C(10) | 1.328(8) |
| W–Cl(1) | 2.422(2) | C(10)–O(2) | 1.254(8) |
| W–Cl(2) | 2.466(2) | C(10)–C(11) | 1.493(8) |
| W–O(1) | 2.142(5) | N(2)–C(21) | 1.379(8) |
| W–N(1)–C(10) | 158.9(5) | N(1)–W–P(2) | 88.5(2) |
| W–N(2)–C(21) | 174.5(5) | N(2)–W–P(2) | 89.1(2) |
| N(1)–W–N(2) | 100.6(2) | N(1)–C(10)–O(2) | 122.8(6) |
| N(1)–W–Cl(1) | 100.2(2) | N(1)–C(10)–C(11) | 116.8(6) |
| N(2)–W–Cl(1) | 100.1(2) | O(2)–C(10)–C(11) | 120.3(6) |

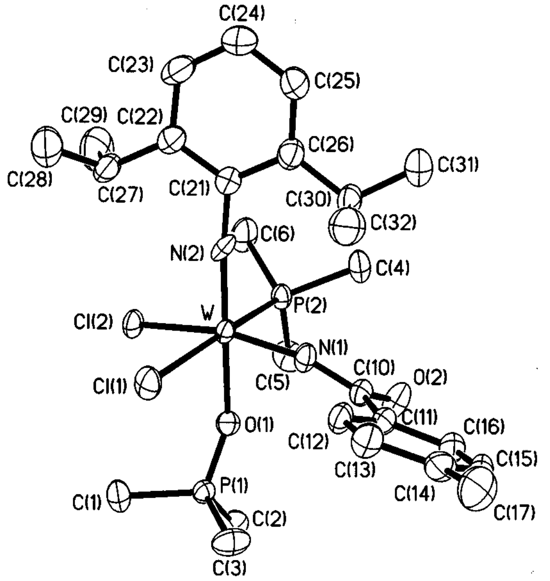


**Fig. 1** Molecular structure of complex **3**; atoms are represented as 50% probability surfaces

bis(organoimide) complexes have been identified where one imido ligand functions as a two-electron donor.[14] For these complexes the M–N–C$_{imido}$ bond angles lie close to 140° which contrasts to the W–N(1)–C(10) bond angle of 158.9(5)° in complex **3**. However W–N–C bond angles are known to be influenced by interligand interactions and crystal packing forces.[15]

The N(1)–C(10), C(10)–O(2) and C(10)–C(11) bond lengths and the bond angles about N(1), C(10), O(2) and C(11) are not significantly different to those found for a variety of uncomplexed organic compounds containing the NCOPh function where the nitrogen lone pair overlaps significantly with the unhybridised *p* orbital of the carbonyl carbon.‡ The muliple-bond nature of the W–N(1) linkage is reflected in complex **3** by the W–Cl(2) bond length [2.466(1) Å] which is significantly longer than the W–Cl(1) bond length [2.422(2) Å] where the chloro ligand lies *trans* to $PMe_3$.

## Theoretical studies

Hartree–Fock (HF) and density-functional (DF) calculations were performed on the model complex $[WCl_2(NMe)(NCOH)(OPH_3)(PH_3)]$ **4** (Fig. 2) in order to study the structure and electronic properties of the two imido ligands. Functional groups like the phenyl group were replaced by simpler ligands in order to manage such large scale *ab-initio* calculations on our SIC R10000 16-processor computer. This technique is commonly applied in quantum theoretical calculations. Structural and electronic differences are expected due to the replacement of delocalising ligands with smaller localised groups. It is therefore relevant to compare the X-ray data with the calculated model structures in some detail to gain information on the accuracy of the various approximations applied.

**Table 2** Selected bond distances (Å) and angles (°) for complexes **3** and **4**

| | X-Ray (**3**) | HF (**4**) | DF (**4**) |
|---|---|---|---|
| W–Cl(1) | 2.422 | 2.491 | 2.434 |
| W–Cl(2) | 2.466 | 2.590 | 2.489 |
| W–N(1) | 1.823 | 1.784 | 1.833 |
| N(1)–C(10) | 1.328 | 1.324 | 1.318 |
| C(10)–O(2) | 1.254 | 1.211 | 1.234 |
| W–N(2) | 1.769 | 1.730 | 1.766 |
| N(2)–C(21) | 1.379 | 1.412 | 1.392 |
| W–P(2) | 2.523 | 2.564 | 2.519 |
| W–O(1) | 2.142 | 2.103 | 2.049 |
| O(1)–P(1) | 1.509 | 1.504 | 1.538 |
| W–N(1)–C(10) | 158.9 | 161.4 | 148.7 |
| N(1)–C(10)–O(2) | 122.8 | 126.0 | 123.2 |
| W–N(2)–C(21) | 174.5 | 174.2 | 173.1 |
| W–O(1)–P(1) | 147.5 | 139.5 | 127.8 |

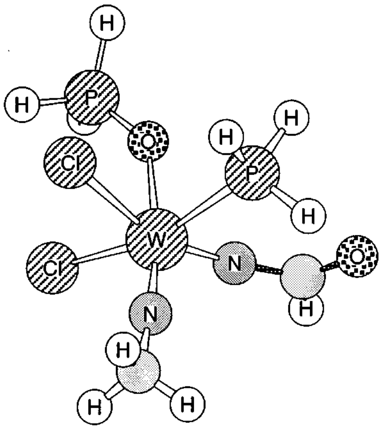


**Fig. 2** Structure of the model complex **4**

The optimised structures at the HF and DF levels are generally in good agreement with the crystal structure (Table 2). For example, $NC_6H_3Pr^i_2$-2,6 is replaced by NMe, and any π delocalisation from the ring onto C(21) and N(2) is therefore eliminated. As a result the N–C bond strength will be reduced in the model complex, and this is perhaps reflected in the longer N(2)–C(21) bond length at both the HF (+0.033 Å) and the DF (+0.013 Å) level of theory. The W–N(2)–C(21) bond angle is reproduced very well by both methods, and the DF W–N(2) distance is only 0.003 Å smaller than the X-ray result, indicating that substitution at the nitrogen has not affected the W–N bonding.

The NCOPh group in **3** has been replaced by NCOH in **4**. The DF W–N(1) and the N(1)-C(10) bond distances are in excellent agreeement with the X-ray structural data despite replacement of the delocalising substituent on C(10) with H which eliminates π delocalisation from the ring substituent across C(10)–O(2) and N(1), thus enhancing the C(10)–O(2) bonding. Indeed, both the HF and DF calculations produce a shorter C(10)–O(2) bond distance than that reported for the crystal structure. We also expect that a positive mesomeric effect from the phenyl ring towards the NCO unit will increase the N–C–C bond angle towards a linear arrangement. However our calculated N–C–H bond angle of 113.4° is significantly smaller than the experimentally determined N–C(10)–C(11)

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‡ A search of the Cambridge Crystallographic Data Centre files shows that the N(1)–C(10) and C(10)–O(2) bond lengths for complex **3** lie on the 3σ limit for the average bond length of 574 compounds containing the function PhCON, while the C(10)–C(11) bond length and the bond angles lie well within this 3σ limit.

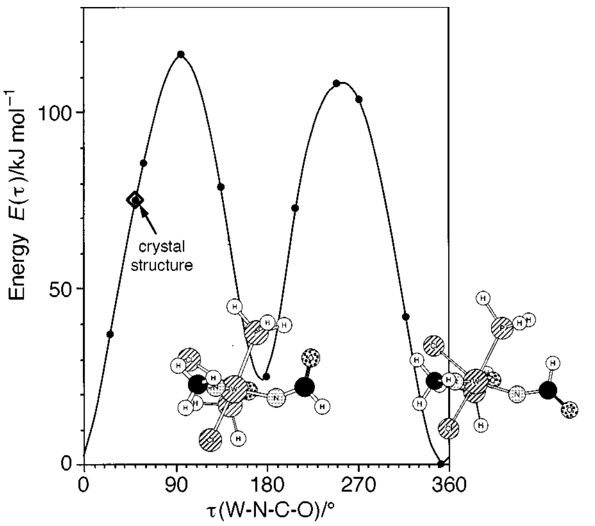


**Fig. 3** Calculated rotation curve for complex **4**

angle of 116.8°. This results in a larger N(1)–C(10)–O(2) angle at both the HF (+3.2°) and DF (+0.4°) level. The W–N(1)–C(10) bond angle at the HF level (161.4°) is very close to the X-ray result (158.9°) indicating that the angle is not influenced by crystal packing forces. Surprisingly the DF method in comparison has a significantly smaller angle (148.7°).

There is a substantial difference of 58° between the X-ray (51°) and calculated (353° ≡ −7°) W–N–C–O torsion angle, $\tau$. The rotation potential curve $E(\tau)$ (Fig. 3) was determined by fixing the structure at the DF optimised geometry and allowing only this torsion angle to vary. No second minimum was located around the X-ray torsion angle of 51° which lies 74.9 kJ mol$^{-1}$ above the global minimium of $E(\tau)$. However, a second minimum was located at the torsion angle of approximately 180°. From these preliminary calculations it is not clear whether the difference between the calculated and the experimentally determined W–N–C–O torsion angles is due to electronic and/or crystal packing effects. For example, at a W–N–C–O torsion angle of −7° the two hydrogens at the NCOH and $PH_3$ ligands are close (2.2 Å). Substitution by $PMe_3$ and NCOPh will therefore lead to significant steric hindrance between the methyl and the phenyl groups. However, this does not explain why a W–N–C–O torsion angle of 180° is not adopted in the solid state.

The $OPMe_3$ ligand of complex **3** is replaced in **4** by $OPH_3$, and lies *trans* to NMe. The W–O(1) bond length is underestimated by both methods (−0.093 Å at the DF level). The O(1)–P(1) bond length is well reproduced at the HF level, but slightly overestimated at the DF level (+0.029 Å). Surprisingly, the W–O(1)–P(1) angle is underestimated by 19.7° at the DF level in stark contrast to the HF method which underestimates this angle by 8.0°. This is consistent with the stronger W–O bond in the model complex compared to that in complex **3** and in agreement with the shorter W–O bond distance obtained at the HF and DF levels. A summary of the differences between the X-ray and DF structures is depicted in Figs. 4 and 5. Fig. 4 shows that in the model structure the P atom of the $OPH_3$ ligand is distorted away from the NCOH ligand; this does not occur in the crystal structure. We can also see that the C atom of the NCOH ligand is not distorted as it is in the crystal structure. In addition, along the *z* axis (Fig. 5) we can see that the C atom of the NCOH ligand is distorted upwards out of the *xy* plane, and that the P atom of the $OPH_3$ ligand is distorted downwards out of the *xy* plane. In the crystal structure the C atom remains undistorted in the plane while the P atom is only slightly distorted out of the plane. Summarising the comparison between the calculated and crystal structures, we find substantial differences at the NCOPh site thus suggesting that the phenyl ligand has a significant effect on the electronic structure of this molecule.

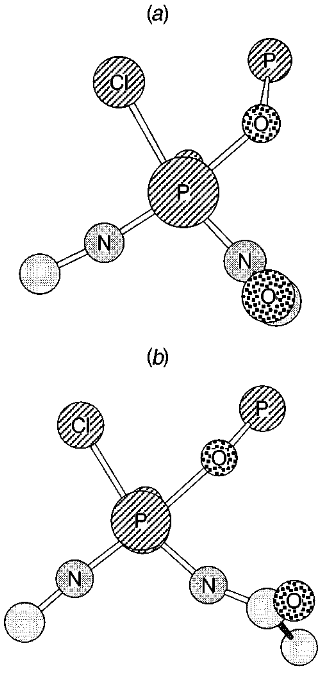
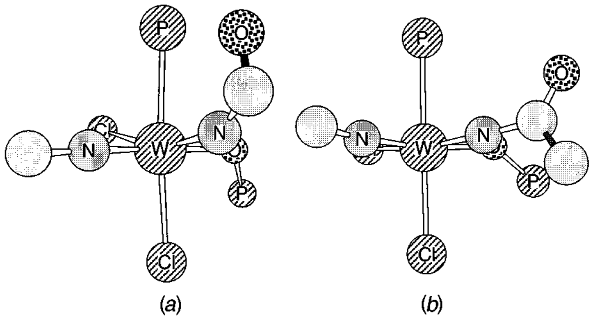


**Fig. 4** Inner co-ordination sphere atoms of the DF structure (*a*) and crystal structure (*b*) in the *xy* plane



(*a*) (*b*)

**Fig. 5** Inner co-ordination sphere atoms of the DF structure (*a*) and crystal structure (*b*) in the *z* direction

Natural bond orbital (NBO) analysis attempts to impose a classical Lewis-type bonding picture upon the invariant electron density and generates hybrid-type bond orbitals.[16] Therefore, it is useful for describing formal oxidation states, which are rather difficult to assess from a delocalised molecular orbital (MO) framework. Key features of this analysis are presented in Tables 3 and 4 and in Fig. 6.

The natural charge on W (+0.78) suggests that the tungsten is in a high oxidation state. The d atomic orbital (AO) populations show that there is extensive orbital intermixing; all of the 5d AOs have populations exceeding 0.9e and the total d AO population is 4.67e. The occupation statistics for W are $5d^{4.74}6s^{0.44}$ at the DF level.

The NMe ligand is formally considered to be a four-electron donor ligand and two of these electrons can be formally identified as the donating lone pair. Indeed, the NBO analysis generates one $\sigma$ and two $\pi$ bonds between the nitrogen s and p AOs and the tungsten d AOs. The resulting W–N bond is slightly ionic because the nitrogen atom contributions dominate (Table 3). As expected, the two $\pi$ bonds are virtually equivalent; the nitrogen contribution is 100% p in character at this level of theory and there is no evidence for a nitrogen lone pair. Both the nitrogen (−0.36) and carbon (−0.56) atoms are negatively charged. Importantly, there is some $\sigma^*$ and $\pi^*$ contribution to the W–N bond, directing electron density towards the tungsten atom.

**Table 3** Density functional NBO population analysis for complex **4**

|  | Natural charge | Bond order* |
|---|---|---|
| W | +0.777 | 3.547 |
| Cl(1) | −0.455 | 0.375 |
| Cl(2) | −0.347 | 0.448 |
| P(1) | +0.232 | 2.798 |
| O(1) | −1.014 | 1.157 |
| P(2) | +1.110 | 3.085 |
| N(2) | −0.355 | 2.137 |
| C(21) | −0.562 | 3.060 |
| H | +0.257 | 0.729 |
| N(1) | −0.486 | 2.048 |
| C(10) | +0.323 | 3.039 |
| O(2) | −0.520 | 1.201 |
| H | +0.137 | 0.696 |

* Atom–atom overlap-weighted NAO bond order, totals by atom.

**Table 4** Density functional NBO bonding analysis for complex **4**

| Bond | % components | Tungsten contribution | antibond occupied |
|---|---|---|---|
| NMe |  |  |  |
| σ W–N | 25–75 | 27% s + 73% d | 0.27 |
| π W–N | 40–60 | 99% d | 0.28 |
| π W–N | 35–65 | 5% p + 94% d | 0.36 |
| σ N–C | 59–41 | — | 0.01 |
| LP N | 100 p | — | 0.00 |
| NCOH |  |  |  |
| σ W–N | 25–75 | 28% s/p + 72% d | 0.35 |
| π W–N | 39–61 | 99% d | 0.25 |
| σ N–C | 62–39 | — | 0.07 |
| σ C–O | 37–63 | — | 0.02 |
| π C–O | 30–70 | — | 0.32 |
| LP O | 52 s–48 p | — | 0.00 |
| LP O | 100 p | — | 0.00 |

LP = Lone pair.

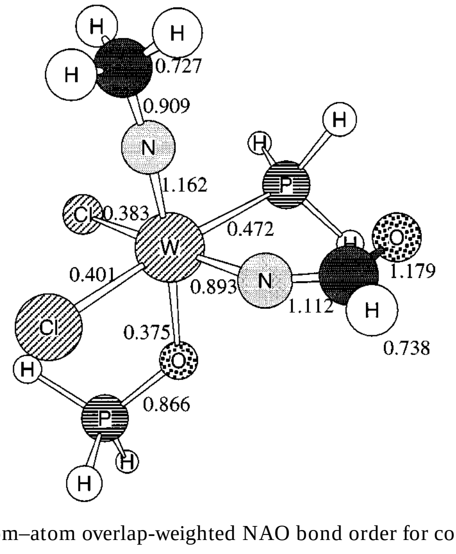


**Fig. 6** Atom–atom overlap-weighted NAO bond order for complex **4**

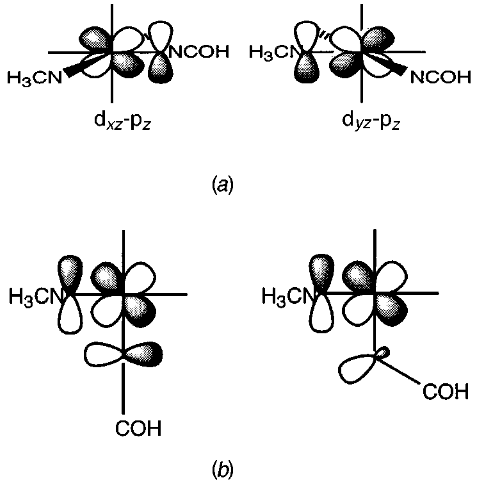


**Fig. 7** Formal interpretation of bonding in the crystal structure of complex **3** in the *xy* plane (*a*) and in the *z* direction (*b*)

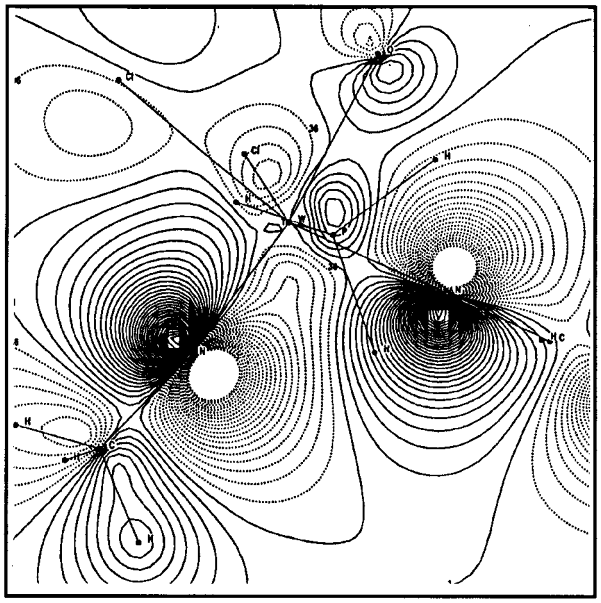


**Fig. 8** The HOMO of complex **4**

The NCOH ligand binds to tungsten *via* one σ and one π bond. The atom–atom overlap weighted NAO (natural atomic orbital) bond order (W–$N_{amide}$ 0.89, W–$N_{imido}$ 1.16) indicates that the W–N bond of the NCOH ligand is weaker than in the imido counterpart due to increased population in the W–N σ* orbital, which again has the effect of relocating more electron density on the tungsten centre. The two nitrogen-containing ligands are competitive π donors and π/σ acceptors. As the NBO analysis reveals, the N in NMe is a better π* acceptor than the N in the NCOH ligand, which accepts mainly *via* the σ* bond. The N–C bond is stronger than the same bond in the NMe ligand (N–$C_{amide}$ 1.11, and N–$C_{imido}$ 0.91). In contrast to the NMe ligand, the NBO analysis located a nitrogen 'lone pair' for the NCOH ligand that is 100% p in character. This orbital overlaps with the C–O π orbitals and introduces some π delocalisation along the entire W–N–C–O backbone; the delocalisation obtained is 8% for tungsten, 4% for the NMe ligand, and more significantly for the carbonyl group; 11% for carbon and 5% for oxygen.

If the NCOH ligand lies on the *x* axis and the NMe ligand on the *y* axis, then the $p_z$ AO of each nitrogen atom interacts with a different d AO on the tungsten atom (Fig. 7). The $p_y$ AO of the NCOH ligand N atom and the $p_x$ AO of the NMe ligand will both compete to interact with the tungsten $d_{x^2-y^2}$ AO. It is possible that one of the nitrogen atoms will dominate in this interaction, causing a localised lone pair to form at the other nitrogen reducing the W–N bond order from three to two and reducing the W–N–C bond angle from 180° in the *xy* plane. Using structural information, the bonding in the complex appears to follow such a pattern. However in the model structure W–N–C bending does not occur in the *xy* plane as in the crystal structure, but in the *xz* plane, hence the bonding in the model complex **4** is not expected to follow this pattern. The canonical valence MOs of this model complex show strong mixing with all the valence AOs and are therefore very delocalised. Nevertheless, we show a two-dimensional plot of the highest occupied molecular orbital (HOMO) in the *xy* plane (Fig. 8) which shows extensive interaction between the two nitrogen ligands in this plane; this MO is bonding with respect to the imido nitrogen but antibonding with respect to the acylimido nitrogen.

## Conclusion

The results of this work demonstrate that $d^0$ and $d^1$ complexes containing *p*-toluonitrile as a four-electron donor $\eta^2$-ligand cannot be prepared using the conventional acetylene-type procedures. Compared to alkynes, the $\pi_\perp$ ($\pi$ perpendicular) orbital of a nitrile is of lower energy which would decrease the stability of an $\eta^2$-nitrile complex relative to the acetylene analogue, especially for electron-deficient metals,[6] so that the $d^0$ and $d^1$ complexes may not exist. However the $d^2$ complex $[WCl_2(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_3]$ **1** is stable and can be prepared from oxidative addition of the nitrile to a $d^4$ complex generated *in situ*. A two-electron donor $\eta^2$-nitrile complex in a $d^2$ electron configuration can be prepared when the imido ligand contains isopropyl groups but not hydrogens, in the 2,6-positions of the phenyl ring. In part, this suggests that an electron-donating imido ligand may be necessary to stabilise $\pi$-back bonding to an $\eta^2$-nitrile ligand. Steric forces are not expected to operate with a single imide of this type.[4] For the bis(imido) complex **3** the crystallographic and theoretical studies show that the electronic properties inherent in the NCO portion of the acylimido ligand only allow essentially a 1$\sigma$, 1$\pi$ interaction of the nitrogen with tungsten so that the bis(imido) function achieves four- and two-electron donor status. The reaction is somewhat unique as it involves oxidative addition of an organonitrile to a $d^2$ tungsten centre resulting in a $d^0$ complex containing an acylimido ligand.

## Experimental

General procedures and instrumentation have been described.[4] Proton, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded at 400, 100 and 162 MHz respectively, in $CDCl_3$. Analytical data were obtained by Dr. A. Cunninghame and associates, University of Otago, New Zealand. The complex $[WCl_4(PMe_3)_3]$ was prepared by treating an excess of $PMe_3$ with $[(WCl_4)_x]$[17] and $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ by the reduction of $[\{WCl_4(NC_6H_3Pr^i_2\text{-}2,6)\}_2]$ using Na/Hg amalgam with $PMe_3$ present.[4] *p*-Toluonitrile (Aldrich) was used as supplied or after drying over and distilling from freshly ground $CaH_2$ granules. Light petroleum (b.p. 40–60 °C), benzene and toluene were distilled from sodium wire and diethyl ether and tetrahydrofuran (thf) from sodium–benzophenone.

### Syntheses

**$[\{WCl_4(NCPh)\}_x]$.** Benzonitrile (0.52 g, 5.0 mmol) in $CH_2Cl_2$ (10 $cm^3$) was added to a suspension of $WCl_6$ (2.0 g, 5.0 mmol) in $CH_2Cl_2$ (60 $cm^3$) containing tetrachloroethylene (2 $cm^3$, 19.23 mmol) and the solution was refluxed for 24 h. The solution was cooled, allowed to stand for 5 h and then filtered and the solvent removed. The extremely air sensitive yellow-brown solid obtained was washed with light petroleum and dried under vacuum. Yield 1.96 g, 91% (Found: C, 20.3, H, 0.9; N, 3.3. $C_7H_5Cl_4NW$ requires C, 19.6; H, 1.2; N, 3.3%).

**$[WCl_2(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe)_3]$ 1.** The complex $[WCl_4(PMe_3)_3]$ (1.0 g, 1.81 mmol) and *p*-toluonitrile (0.22 g, 1.88 mmol) in thf (50 $cm^3$) were added to sodium–mercury amalgam (0.084 g, 3.65 mmol; 35 g Hg) under thf (20 $cm^3$) and the mixture was stirred vigorously for 3 h. The solution was filtered, the solvent removed and the green gum extracted with diethyl ether. The solution was filtered and the solvent removed to give the complex as a green flaky material. Crude yield 0.78 g, 72%. The analytically pure sample was obtained by extracting the crude sample with light petroleum (200 $cm^3$). The solution was filtered, allowed to stand overnight, filtered again, and the volume reduced to *ca.* 100 $cm^3$. On standing at room temperature and then at −20 °C emerald-green crystals of the complex formed. Yield 0.41 g, 38% (Found: C, 33.7; H, 5.7; N, 2.3. $C_{17}H_{34}Cl_2NP_3W$ requires C, 34.0; H, 5.7; N, 2.3%). NMR: $^1H$, $\delta$ 1.12 [d, $^2J(HP)$ 8.7, 9 H, $PMe_3$], 1.72 [t, $^2J(HP)$ 6.8, 18 H, $PMe_3$], 2.48 (s, 3 H, Me), 7.34 [d, $^3J(HH)$ 7.7, 2 H, *m*-H] and 7.77 [d, $^3J(HH)$ 7.7, 2 H, *o*-H]; $^{13}C\text{-}\{^1H\}$, $\delta$ 16.3 [t, $^1J(CP)$ 26.3, $PMe_3$], 19.7 (Me), 22.5 [d, $^1J(CP)$ 29.7 Hz, $PMe_3$], 127.6 and 128.3 (aromatic CH), 136.9 (*ipso*-C) and 138.4 (*p*-C), 232.2 (m, C≡N).

**$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(\eta^2\text{-}NCC_6H_4Me\text{-}4)(PMe_3)_2]$ 2.** (*a*) *p*-Toluonitrile (0.2 g, 1.7 mmol) in toluene (10 $cm^3$) was added to $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ (1.0 g, 1.5 mmol) in toluene (30 $cm^3$) and the mixture was refluxed for 4 h. The yellow-brown solution was filtered, the solvent removed and the resulting gum washed with light petroleum until solidification occurred. Yield 1.0 g, 94% (Found: C, 43.7; H, 6.1; N, 4.6. $C_{26}H_{42}Cl_2N_2P_2W$ requires C, 44.7; H, 6.1; N, 4.6%). NMR: $^1H$, $\delta$ 0.88 (d, 3 H, Me), 0.94 (d, 3 H, Me), 1.15 (partially resolved doublet, 6 H, 2Me), 1.42 and 1.69 [2d, $^2J(HP)$ 9.9, 18 H, $PMe_3$], 2.38 (s, 3 H, Me), 2.52 (spt, 1 H, CH), 4.41 (spt, 1 H, CH), 6.90 (br t, 1 H, *p*-H), 7.02 (br d, 2 H, *m*-H), 7.25 [d, $^3J(HH)$ 7.7, 2 H, *m*-H] and 7.51 [d, $^3J(HH)$ 7.7, 2 H, *o*-H]; $^{13}C\text{-}\{^1H\}$, $\delta$ 12.2 and 14.1 [2d, $^1J(CP)$ 30.0, $PMe_3$], 21.2 (Me), 22.3, 23.6, 25.0 and 25.3 (Me), 26.7 and 26.8 (CH), 122.5 (*m*-$C_{\mathbf{imido}}$), 123.4 (*p*-$C_{\mathbf{imido}}$), 127.7 (*o*-$C_{\mathbf{nitrile}}$), 129.6 (*m*-$C_{\mathbf{nitrile}}$), 135.9 [d, $^3J(CP)$ 4.0, *ipso*-$C_{\mathbf{nitrile}}$], 139.4 ($C_{\mathbf{nitrile}}$), 148.5 (partially resolved triplet, *ipso*-$C_{\mathbf{imido}}$), 149.1 and 149.5 (*o*-$C_{\mathbf{imido}}$), 178.8 and 178.9 [dd, $^2J(CP)_{cis}$ 2.8, $^2J(CP)_{trans}$ 12.4, C≡N]; $^{31}P\text{-}\{^1H\}$, $\delta$ –19.4 [d, $^2J(PP)$ 183.3, $^1J(PW)$ 242.5] and –11.6 [d, $^2J(PP)$ 183.3, $^1J(PW)$ 253.1 Hz].

(*b*) The complex $[WCl_3(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_2]$ (0.6 g, 0.97 mmol) in benzene (40 $cm^3$) was added to *p*-toluonitrile (0.12 g, 1.0 mmol) in benzene (20 $cm^3$) over sodium–mercury amalgam (0.023 g, 1.0 mmol Na; 20 g Hg) and the mixture was stirred vigorously for 3 h. The solution was filtered and the solvent removed to give a gum which on standing under light petroleum (40 $cm^3$) gave the complex as a yellow solid. Yield 0.61 g, 90%.

**$[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(NCOC_6H_4Me\text{-}4)(OPMe_3)(PMe_3)]$ 3.** Unpurified *p*-toluonitrile (0.2 g, 1.7 mmol) in toluene (10 $cm^3$) was added to $[WCl_2(NC_6H_3Pr^i_2\text{-}2,6)(PMe_3)_3]$ (1.0 g, 1.5 mmol) in toluene (30 $cm^3$) and the mixture was refluxed for 4 h. After filtering the solution and removing the solvent, NMR spectroscopy indicated the presence of **2** and an additional complex. The gummy material was taken up in toluene (20 $cm^3$), the volume reduced to about one-half and the solution carefully layered with light petroleum (50 $cm^3$). On standing for several weeks a small quantity of yellow crystals formed which NMR spectroscopy indicated were solvated with less than 1 equivalent of toluene [Found: C, 46.3; H, 6.5; N, 3.5. $C_{31}H_{48}Cl_2N_2O_2P_2W$ (*i.e.* $C_{26}H_{42}Cl_2N_2O_2P_2W\cdot\frac{5}{7}C_7H_8$) requires C, 46.7; H, 6.1; N, 3.8%]. NMR: $^1H$, $\delta$ 1.23 [d, $^3J(HH)$ 6.2, 12 H, Me], 1.47 [d, $^2J(HP)$ 12.9, 9 H, $PMe_3$], 2.03 [d, $^2J(HP)$ 24.6 Hz, 9 H, $OPMe_3$], 2.34 (s, 3 H, Me), 3.59 (spt, 2 H, CH), 7.08–7.25 (m, 5 H, *m*- and *p*-$H_{\mathbf{imido},}$ *m*-$H_{\mathbf{acylimido}}$) and 7.65 (d, *o*-$H_{\mathbf{acylimido}}$); $^{13}C\text{-}\{^1H\}$, $\delta$ 17.4 ($PMe_3$), 18.1 ($OPMe_3$), 21.2 (Me), 23.7 (isopropyl Me), 28.0 (CH), 123.8 (*o*-$C_{\mathbf{acylimido}}$), 127.2 (*m*-$C_{\mathbf{imido}}$), 128.9 (*m*-$C_{\mathbf{acylimido}}$), 129.0 (*p*-$C_{\mathbf{imido}}$), 141.3, 140.4 and 140.4 (*p*-$C_{\mathbf{acylimido}}$, *o*- and *ipso*-$C_{\mathbf{imido}}$), 142.1 (*ipso*-$C_{\mathbf{acylimido}}$) and 169.0 (C=O); $^{31}P\text{-}\{^1H\}$, $\delta$ −15.6 (s, $PMe_3$) and – 3.2 (s, $OPMe_3$).

### Crystallography

Crystal data for complex **3** are given in Table 5, together with information on instrumentation, data collection and structure determination. Unit-cell parameters were determined by least-squares fit to the four-circle coordinates of 25 reflections centred on a Nonius CAD-4 diffractometer. The data were collected at 193 K with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ 0.710 69 Å) and corrected for Lorentz-polarisation effects. Empirical absorption corrections were applied using $\psi$ scans.[18] The structure was solved by Patterson and Fourier

**Table 5** Crystallographic data for complex **3**

| | |
|---|---|
| Formula | $C_{26}H_{42}Cl_2N_2O_2P_2W$ |
| $M$ | 731.31 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$/Å | 18.480(3) |
| $b$/Å | 10.876(3) |
| $c$/Å | 18.467(5) |
| β/° | 92.55(2) |
| $U$/Å$^3$ | 3708(2) |
| $Z$ | 4 |
| $D_c$/g cm$^{-3}$ | 1.310 |
| $F$(000) | 1464 |
| μ/mm$^{-1}$ | 3.37 |
| Scan technique | ω–2θ |
| 2θ Range/° | 1–26 |
| $h,k,l$ Ranges | $-22 \leqslant h \leqslant 0,\ -13 \leqslant k \leqslant 0,\ -22 \leqslant l \leqslant 22$ |
| No. reflections | 7546 ($R_{int}$ 0.0463) |
| No. observed reflections [$I > 2\sigma(I)$] | 7219 |
| Crystal size/mm | 0.12 × 0.22 × 0.28 |
| Minimum, maximum absorption correction | 0.679, 0.997 |
| Least-squares weights $a$, $b$ | 0.088, 7.54 |
| No. variables | 327 |
| Goodness of fit on $F^2$ | 1.185 |
| Function minimised | $\Sigma w(F_o^2 - F_c^2)^2$ |
| $R1$ (observed data), $wR2$ (all data) | 0.0475, 0.1338 |
| Maximum, minimum peak heights in final density map/e Å$^{-3}$ | +2.87, −2.23 |

$R = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1.0/[\sigma^2(F_o^2) + aP^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

techniques and refined by full-matrix least squares on $F^2$. Structure factors were for neutral atoms and all data were included in the refinement using SHELXL 93.[19] All atoms, other than hydrogen, were allowed to assume anisotropic thermal motion. Hydrogen atoms were located geometrically and allowed to ride on the atoms to which they were attached with 20% higher thermal parameter.

CCDC reference number 186/624.

## Theoretical

Hartree–Fock and density-functional calculations were performed on the model complex $[WCl_2(NMe)(NCOH)(OPH_3)(PH_3)]$ **4**. The program GAUSSIAN 92[20] was used for all calculations. The Slater exchange functional and Vosko, Wilk and Nusair 1980 correlation functional were used in the DF calculation.[21,22] Non-relativistic pseudo-potentials and associated basis sets (decontracted) were used for chlorine {[4s4p/3s3p] and phosphorus [4s4p + (1d)]/[3s3p + (1d)]}; for tungsten a scalar-relativistic pseudo-potential and a [8s7p6d]/[6s5p3d] basis set was used.[2] All-electron 6-311G basis sets were specified for C, O and N, and for H a STO-3G basis set was used.[2] A full geometry optimisation using no symmetry constraints was carried out at both levels of theory. The single reference HF contains no electron correlation (by definition) whereas the DF theory includes dynamic correlation effects and should therefore be more suitable for calculations on transition element-containing compounds. Therefore an NBO analysis[16,23] was carried out on the self consistant field (SCF) density at the DF level. In addition, two-dimensional MO plots using the MOLDEN program[24] were generated.

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