Metal Centres Linked by Bis(imido)phenylene Ligands. Synthesis and X-ray Crystal Structures of 1,3- and 1,4-[{*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)$}$_2$(μ-NC_6H_4N)]

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Addition of 2 equiv. of [$WCl_2(Ph_2PMe)_4$] to 1,3- or 1,4-phenylenediisocyanate results in rapid oxidative addition of isocyanate affording the bis(imido)phenylene bridged tungsten(IV) complexes 1,3- and 1,4-[{*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)$}$_2$(μ-NC_6H_4N)], respectively; both have been characterised by X-ray crystallography.

Linking transition metal centres together with ligands possessing a delocalised π-system allows communication between them, leading to novel physical properties. Classically, ligands such as pyrazine and 4,4′-bipyridine have found extensive use in this context as exemplified by the archetypal Creutz–Taube system.[1] The binding of imido ligands to transition metal centres is well known and occurs for metals in a variety of oxidation states, although high valent centres in which the metal has a d^0–d^2 electronic configuration are particularly stable.[2] This ligation is desirable for the design of π-conjugated sytems containing metal atoms since strong interactions occur between the metal d-orbitals and p-orbitals on nitrogen. Thus joining metal centres together with two imido functionalities linked *via* an unsaturated organic moiety, such as an aryl ring, will lead to a fully conjugated π-system. To date this has only been achieved on a handful of occasions using the bis(imido)phenylene ligand.[3–7] Herein we report the first examples in which organometallic centres are linked *via* bis(imido)phenylene ligands. We have achieved this by utilising the oxidative addition of commercially available phenylenediisocyanates to a tungsten(II) centre.

Mayer and coworkers have recently shown that isocyanates readily undergo oxidative addition to the tungsten(II) centre in

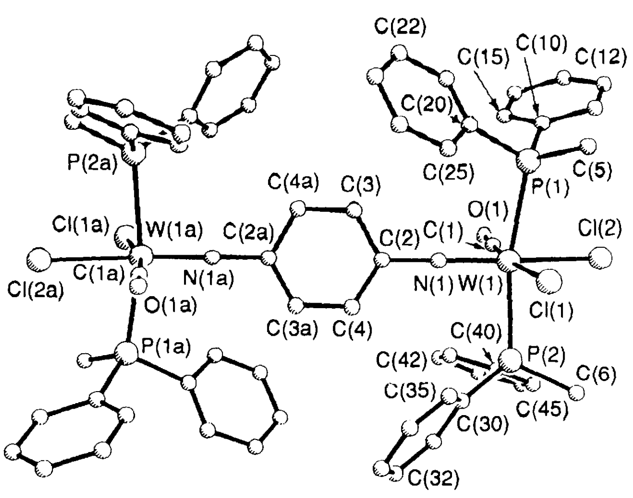

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.528(2), W(1)–P(2) 2.536(2), W(1)–Cl(1) 2.446(2), W(1)–Cl(2) 2.465(2), W(1)–N(1) 1.743(5), W(1)–C(1) 1.991(8), N(1)–C(2) 1.390(8), C(1)–O(1) 1.145(11); P(1)–W(1)–P(2) 167.8(1), Cl(1)–W(1)–Cl(2) 90.0(1), W(1)–N(1)–C(2) 173.2(4).

[$WCl_2(PPh_2Me)_4$].[8] In a simple extension of this reaction, addition of 2 equiv. of [$WCl_2(PPh_2Me)_4$] to a toluene solution of the phenylenediisocyanate resulted in the formation of green 1,4-[{*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)$}$_2$(μ-NC_6H_4N)] **1** and pink 1,3-[{*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)$}$_2$(μ-NC_6H_4N)] **2** as the only reaction products. Both were characterised by elemental analyses and spectroscopic techniques.† Oxidative addition of the nitrogen–carbon bond of the isocyanate was confirmed by the presence of a carbonyl absorption in the IR spectrum of both **1** (1968 cm^{-1}) and **2** (1966 cm^{-1}), while ^{31}P NMR data suggested that the remaining phosphines adopted a *trans* disposition. In order to confirm the nature of these products and elucidate any structural differences, X-ray crystal structures were carried out for both. The results are shown in Figs. 1–3.‡

Superficially, the two structures are very similar. Both contain two approximately octahedral tungsten(IV) centres linked *via* the bis(imido)phenylene ligands. Each octahedral centre contains a *trans* disposition of phosphine ligands and a *cis* arrangement of chlorides. The tungsten–chloride bond lengths are similar despite the fact that one is *trans* to the imido ligand [**1** W(1)–Cl(2) 2.446(2); **2** W(1)–Cl(2) 2.462(2), W(2)–Cl(4) 2.460(3) Å], and the second *trans* to a carbonyl [**1** W(1)–Cl(1) 2.466(2); **2** W(1)–Cl(1) 2.469(2), W(2)–Cl(3) 2.473(2) Å]. The carbonyls bound to tungsten are essentially linear with tungsten–carbon bond lengths being within the expected range. The metal centres in both are linked *via* the bis(imido)phenylene ligands, the short metal–nitrogen distances being typical (**1** W(1)–N(1) 1.744(5); **2** W(1)–N(1) 1.751(6), W(2)–N(2) 1.766(6) Å], while the bond angles at nitrogen indicate a substantial π-interaction [**1** W(1)–N(1)–C(2) 173.2(4); **2** W(1)–N(1)–C(3) 172.8(6), W(2)–N(2)–C(5) 172.4(5)°].[2] In both structures the carbon–carbon bonds within the aryl ring do not vary significantly within experimental error, indicating that there is no localisation of π-interactions. Similarly, the nitrogen–carbon bond lengths are similar to those found in related arylimido complexes [**1** N(1)–C(2) 1.390(8); **2** N(1)–C(3) 1.399(10), N(2)–C(5) 1.382(11) Å].[2]

Three major differences arise between the two structures relating to: the arrangement of octahedral tungsten centres with respect to one another, the torsional angle between them, and the orientation of the aryl ring with respect to these centres. Thus, while in **1** the tungsten centres are orientated such that the carbonyl groups lie on opposite sides of the molecule (*trans*), in **2** they lie on the same side (*cis*), and point in the direction of the major part of the aryl ring. The second difference is that while in **1** the two octahedral centres are eclipsed (imposed by crystal symmetry), in **2** they are twisted by approximately 7.4° with respect to one another. This may be a result of steric interactions between the bulky methyldiphenylphosphine ligands on adjacent metal centres, however orientation of the methyl groups towards one another would minimise this. Thus, if steric effects are important it is surprising that this rotomer is favoured in the solid-state. The third, and probably most important difference in view of π-conjugation, is the orientation of the aryl ring with respect to the metal centres. Thus, while in **1** the aryl ring lies almost perpendicular to the plane containing the chlorides and carbonyl (torsional angle 80.2°), in **2**, while the complex is slightly more distorted, the aryl ring essentially lies in this plane (torsional angles 5.8 and 23.9°).

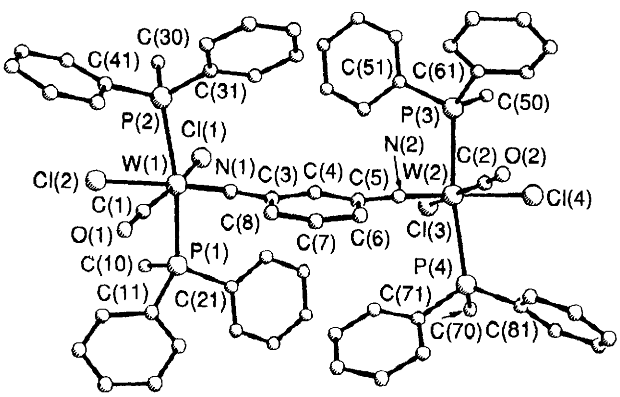

Fig. 2 Selected bond lengths (Å) and angles (°): W(1)–P(1) 2.531(2), W(1)–P(2) 2.537(2), W(1)–Cl(1) 2.469(2), W(1)–Cl(2) 2.462(2), W(1)–N(1) 1.751(6), W(1)–C(1) 1.993(9), W(2)–P(3) 2.541(2), W(2)–P(4) 2.537(2), W(2)–Cl(3) 2.473(2), W(2)–Cl(4) 2.460(3), W(2)–N(2) 1.766(6), W(2)–C(2) 1.997(9), N(1)–C(3) 1.399(10), N(2)–C(5) 1.381(10), C(1)–O(1) 1.156(11), C(2)–O(2) 1.158(11); P(1)–W(1)–P(2) 167.3(1), P(3)–W(2)–P(4) 167.5(1), Cl(1)–W(1)–Cl(2) 90.7(1), Cl(3)–W(2)–Cl(4) 91.0(4), W(1)–N(1)–C(3) 172.8(6), W(2)–N(2)–C(5) 172.4(5).

The structures of two other complexes containing bis(imido)phenylene linked transition metal centres have previously been elucidated crystallographically. Thus, Errington and coworkers have structurally characterised a tungsten(V) dimer closely related to **1**, namely 1,4-[{*mer,trans*-$WCl_3(PhPMe_2)_2$}$_2$(μ-NC_6H_4N)].[6] The most notable differences between the two structures is that in the latter in the aryl ring lies approximately in the plane of the chlorides (average torsional angle 26.3°), that is rotated almost 90° with respect to that found in **1**. No example of a 1,3-linked system has been reported, however Wilkinson and coworkers have structurally characterised the *ortho*-bis(imido)phenylene complex 1,2-[{*mer*-$WCl_3(\eta^2$-1,2-$HNC_6H_4NH_2)$}$_2$(μ-NC_6H_4N)].[7]

The orientation of the bis(imido)phenylene moiety with the metal centres it links is anticipated to have a pronounced effect upon the degree of π-conjugation, and thus the physical properties of complexes of this type. Mayer and coworkers have previously characterised the related monomeric complex [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)(N$-*p*-Tol)] crystallographically.[8] Generally structural features are very similar to those found in **1** and **2**, however, like the linked tungsten(V) dimer, the aryl ring lies close to the plane of the chlorides and carbonyl. This is again in contrast to the orientation adopted in **1**. In light of the structural characterisation of both **1** and **2**, it is difficult to see how steric effects would influence this, and although **1** crystallises with a molecule of chlorobenzene in the lattice, no short intermolecular contacts are observed. It thus appears that there must be an electronic preference for this conformation. We are not certain what the cause of this electronic effect

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† *Spectroscopic data.* **1**: ^1H NMR ($CDCl_3$) δ 7.37–7.09 (m, 44 H, Ph), 2.44 (t, *J* 3.9 Hz, 12 H, Me); ^{31}P NMR ($CDCl_3$) δ 2.08 (s, J_{PW} 290 Hz); IR (CH_2Cl_2) 1968 (CO) cm^{-1}. **2** ^1H NMR ($CDCl_3$) δ 7.78–7.15 (m, 44 H, Ph), 2.27 (t, *J* 3.9 Hz, 12 H, Me); ^{31}P NMR ($CDCl_3$) δ 2.14 (s, J_{PW} 290 Hz); IR (CH_2Cl_2) 1966 (CO) cm^{-1}. Satisfactory elemental analyses were obtained.

‡ *Crystal data*: For both structures intensity data were collected on crystals mounted on a Nicolet R3mV diffractometer. The structure of **1** was solved by heavy atom methods, while **2** was solved by direct methods. For **1**·C_6H_5Cl: $W_2Cl_5P_4O_2N_2C_{66}H_{61}$, $M = 1583.12$, triclinic, space group $P\bar{1}$, $a = 10.128(1)$, $b = 11.555(3)$, $c = 14.754(3)$ Å, $\alpha = 102.28(2)$, $\beta = 97.36(1)$, $\gamma = 91.77(2)°$, $V = 1669.5(6)$ Å^3, $Z = 1$, $T = 292$ K, $D_c = 1.57$ g cm^{-3}, $F(000) = 780$, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 38.53 cm^{-1}, crystal size = 0.40 × 0.36 × 0.30 mm, data with $I \geqslant 3\sigma(I) = 3059$, parameters = 338, $R = 0.039$, $R_w = 0.044$.

For **2**: $W_2Cl_4P_4O_2N_2C_{60}H_{56}$, $M = 1470.56$, monoclinic, space group $P2_1/a$, $a = 15.681(3)$, $b = 22.175(2)$, $c = 17.062(5)$ Å, $\beta = 92.06(2)°$, $V = 5929.01(2.23)$ Å^3, $Z = 4$, $T = 292$K, $D_c = 1.65$ g cm^{-3}, $F(000) = 2888$, $\lambda = 0.071073$ Å, μ(Mo-Kα) = 42.91, crystal size = 0.64 × 0.46 × 0.40 mm, data with $I \geqslant 3\sigma(I) = 7353$, parameters = 667, $R = 0.041$, $R_W = 0.038$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

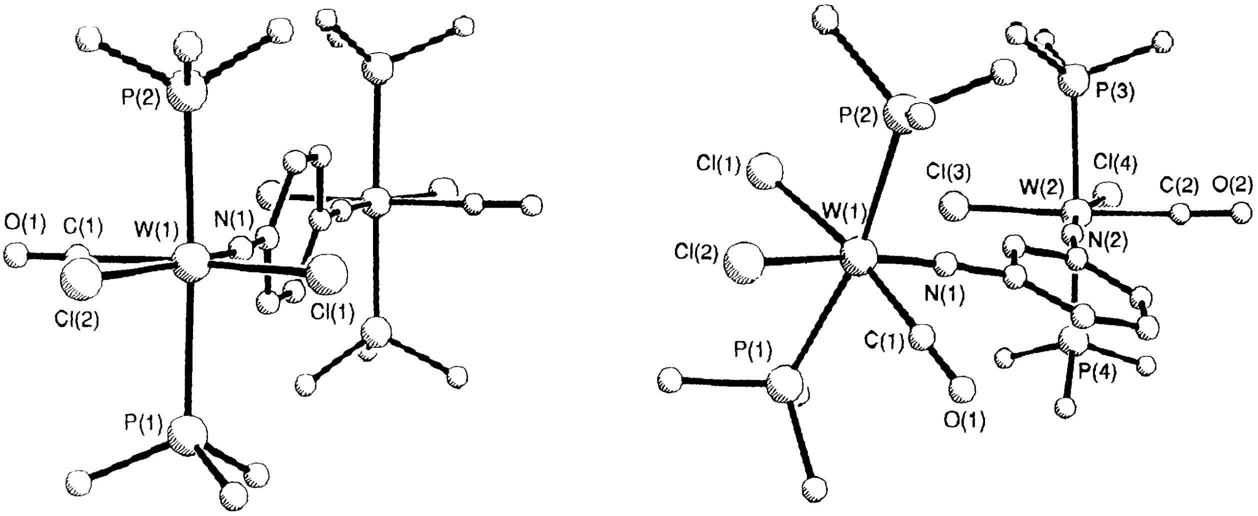

Fig. 3 The central core geometries of **1** and **2**

is, however it is noteworthy that possible conjugation between the metal centre and aryl ring will be maximised when the latter lies in the plane of the chlorides and carbonyl, or when rotated by 90° with respect to this position. Thus the conformational difference between **1** and the tungsten(v) dimer[6] might not be particularly significant.

Structural characterisation of isomers **1** and **2** suggests that small positional changes may lead to quite different structural configurations. Studies on the organometallic uranium complexes show that such positional differences may also lead to quite different physical properties. Hence both the 1,3- and 1,4-isomers of $[\{U(MeC_5H_4)_3\}_2(\mu\text{-}NC_6H_4N)]$ have been synthesised. While in the 1,4-isomer antiferromagnetic coupling of uranium centres occurs at low temperatures, no coupling is observed in the 1,3-isomer. This coupling has been attributed to a superexchange pathway, a process which is not possible in the 1,3-isomer.[5] We are currently investigating the electrochemical and non-linear optical properties of both **1** and **2**, and a number of related bis(imido)phenylene linked metal centres, in order to determine the degree of π-conjugation between them, and the effect of positional isomerism.

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