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Cleaving carbon–carbon bonds by inserting tungsten into unstrained aromatic rings

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The cleavage of C–H and C–C bonds by transition metal centres is of fundamental interest and plays an important role in the synthesis of complex organic molecules from petroleum feedstocks[1–6]. But while there are many examples for the oxidative addition of C–H bonds to a metal centre, transformations that feature oxidative addition of C–C bonds are rare. The paucity of transformations that involve the cleavage of C–C rather than C–H bonds is usually attributed to kinetic factors arising from the greater steric hindrance and the directional nature of the sp^n hybrids that form the C–C bond, and to thermodynamic factors arising from the fact that M–C bonds are weaker than M–H bonds[2–5]. Not surprisingly, therefore, most examples of C–C bond cleavage either avoid the kinetic limitations by using metal compounds in which the C–C bond is held in close proximity to the metal centre, or avoid the thermodynamic limitations by using organic substrates in which the cleavage is accompanied by either a relief of strain energy or the formation of an aromatic system[2–5]. Here, we show that a tungsten centre can be used to cleave a strong C–C bond that is a component of an unstrained 6-membered aromatic ring. The cleavage is enabled by the formation of an unusual chelating di(isocyanide) ligand, which suggests that other metal centres with suitable ancillary ligands could also accomplish the cleavage of strong C–C bonds of aromatic substrates and thereby provide new ways of functionalizing such molecules.

We are currently developing the coordination chemistry of molybdenum with respect to heterocyclic aromatic nitrogen compounds to acquire a more detailed understanding of the reactions involved in hydrodenitrogenation, the important process by which nitrogen is removed from compounds in fossil fuels[7,8]. As part of these investigations, we reported that quinoxaline (QoxH) reacts with electron-rich $Mo(PMe_3)_6$ to give $(\eta^2\text{-}N,C\text{-Qox})Mo(PMe_3)_4H$ via oxidative addition of a C−H bond, and further demonstrated that this complex converts sequentially to $(\eta^6\text{-}C_4N_2\text{-QoxH})Mo(PMe_3)_3$ and $(\eta^6\text{-}C_6\text{-QoxH})Mo(PMe_3)_3$ in which the quinoxaline ligand coordinates in an η^6 manner through the heterocyclic and carbocyclic rings, respectively (Fig. 1)[8]. (Here italics indicate the coordinating atoms.) Seeking to discover a system that would achieve cleavage of a C–N bond of the aromatic ring, we explored tungsten compounds because this metal shows a greater ability to accomplish bond cleavage via oxidative addition than does molybdenum[9].

As illustrated in Fig. 1, the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with QoxH indeed proceeds very differently to that for the molybdenum system (see Supplementary Information for experimental details regarding synthesis and compound characterization). Thus, instead of tungsten simply coordinating QoxH in an η^6 manner, $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ reacts with QoxH either (1) to induce C–C bond cleavage and dehydrogenation to give $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$, or (2) to form the dihydride complex $(\eta^4\text{-}C_2N_2\text{-QoxH})W(PMe_3)_3H_2$ (15% and 24% yields, respectively, after 18 h at 90 °C). The dihydride complex does not convert to $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$ under the reaction conditions. The transformations observed for QoxH are also observed for 6-methylquinoxaline ($Qox^{Me}H$) and 6,7-dimethylquinoxaline ($Qox^{Me_2}H$), thereby demonstrating the generality of the reactions (see Supplementary Information).

In addition to the dihydride $(\eta^4\text{-}C_2N_2\text{-QoxH})W(PMe_3)_3H_2$, the tetrahydride $W(PMe_3)_4H_4$ is also formed in low yield (<5%) during the course of the reaction. Although an obvious source for the hydride ligands of these complexes is the H_2 that is liberated during the formation of $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$, we note that the conversion of QoxH to 2,2′-biquinoxaline, $(2,2'\text{-Qox})_2$ (identified by X-ray diffraction, see Supplementary Fig. 3) may also serve as a source of H_2. Not unexpectedly, the yield of $(\eta^4\text{-}C_2N_2\text{-QoxH})W(PMe_3)_3H_2$ (86%),

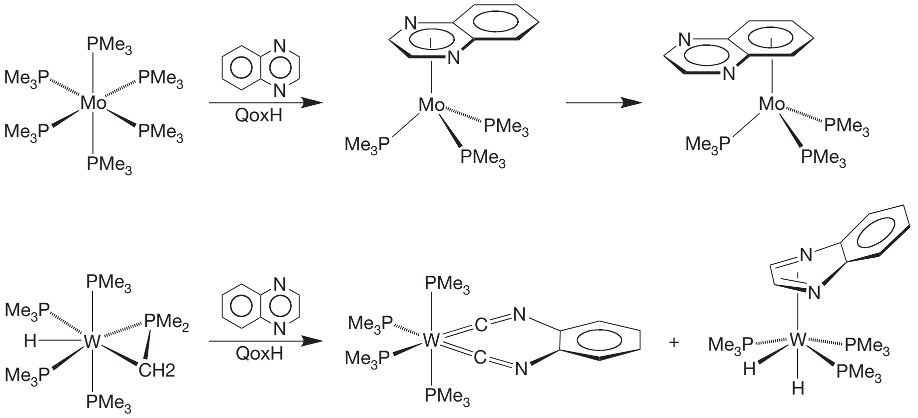

Figure 1 | Different reactivity of quinoxaline towards $Mo(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$.

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relative to that of $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$, increases considerably if the reaction between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and QoxH is performed under an atmosphere of H_2 (see Supplementary Information).

The dihydride complexes $(\eta^4\text{-}C_2N_2\text{-}Qox^{R_2}H)W(PMe_3)_3H_2$ (where R_2 = H, H; Me, H; or Me, Me) represent unprecedented examples of η^4-coordination of this dinuclear aromatic compound via the heterocyclic ring, as clearly seen from the structure of $(\eta^4\text{-}C_2N_2\text{-}Qox^{Me_2}H)W(PMe_3)_3H_2$ shown in Fig. 2. As such, $(\eta^4\text{-}C_2N_2\text{-}Qox^{R_2}H)W(PMe_3)_3H_2$ provide important new structural motifs for the means by which heterocyclic nitrogen compounds may bind to the surface of hydrodenitrogenation catalysts.

The most significant aspect of the reactions between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and $Qox^{R_2}H$, however, pertains to the formation of $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$: as is evident from the structure of $[\kappa^2\text{-}C_2\text{-}C_6H_2Me_2(NC)_2]W(PMe_3)_4$ in Fig. 3, the formation of these compounds requires the breaking of an aromatic C–C bond that is substantially stronger than a typical C–C single bond[10]. Remarkably, this unprecedented cleavage of the aromatic C–C bond takes place in preference to that of the C–N bond. The latter bond might have been expected to be more reactive because the cleavage of the C-N bond in pyridine[11] and its derivatives[12–15] has been achieved by various metal centres, thereby making the cleavage of the C–C bond in the present system all the more remarkable.

The cleaved quinoxaline fragments within $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$, namely $C_6H_2R_2(NC)_2$, correspond to known di(isocyanide) compounds[16]. As such, $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$ may be viewed as simple transition-metal isocyanide complexes of the type $ML_4(CNR)_2$ for which there is precedent. However, the $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$ complexes exhibit several interesting structural features. For example, whereas the majority of transition-metal isocyanide compounds have almost linear C–N–C bond angles (the mean C–N–C bond angle for isocyanide compounds listed in the Cambridge Structural Database (Version 5.30) is 172°), the geometries at nitrogen in each of the $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$ complexes are severely bent (125–128°). Such bending, which has also been observed for some monodentate isocyanide complexes[17], is consistent with considerable metal-to-ligand π-backbonding so that W=C=N–R is a better description of the interaction than is $W{\leftarrow}C^-{\equiv}N^+\text{–}R$ (ref. 18). Further evidence for the multiply bonded nature of the W–C interactions in $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$ is the observed average W–C bond length of 1.93 Å, which compares favourably with the mean value of 1.98 Å for structurally characterized compounds with $W{=}CR_2$ double bonds listed in the Cambridge Structural Database (Version 5.30), but is much shorter than the mean W–C single bond length of 2.23 Å.

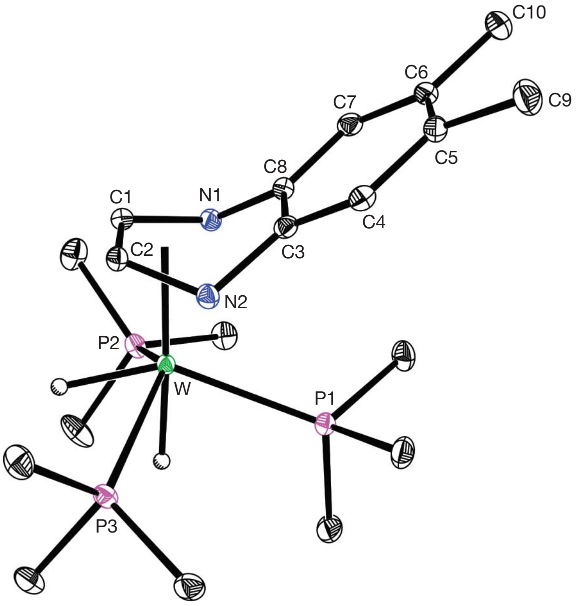

Figure 2 | Molecular structure of $(\eta^4\text{-}C_2N_2\text{-}Qox^{Me_2}H)W(PMe_3)_3H_2$.

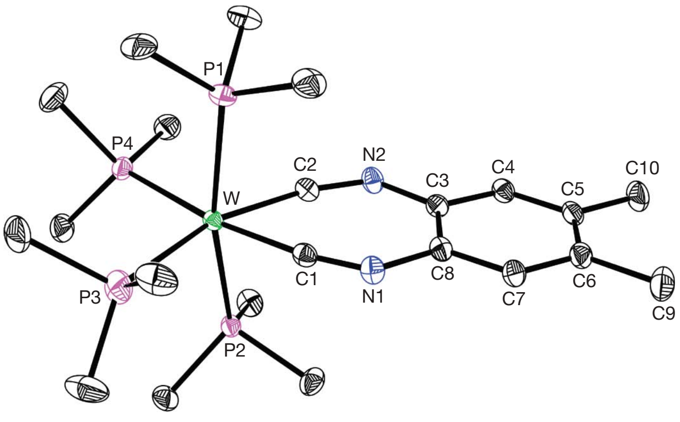

Figure 3 | Molecular structure of $[\kappa^2\text{-}C_2\text{-}C_6H_2Me_2(NC)_2]W(PMe_3)_4$.

A high degree of backbonding is also suggested by the ν(CN) stretching frequencies of $[\kappa^2\text{-}C_2\text{-}C_6H_2R_2(NC)_2]W(PMe_3)_4$ ranging from 1,698–1,709 cm^{-1} (see Supplementary Information), which is at the low end for transition-metal isocyanide complexes; for comparison, ν(CN) for isocyanide complexes span a range of at least 2,310 cm^{-1} to 1,670 cm^{-1} (refs 19, 20). Similarly, the ^{13}C nuclear magnetic resonance (NMR) spectroscopic signals of transition-metal isocyanide compounds span at least 151.8–238.7 parts per million (p.p.m.) (refs 20, 21), with the compound having the most downfield chemical shift, namely $[Fe(CNXyl)_4]^{2-}$, having the lowest ν(CN) stretching frequency and a highly bent C–N–C bond angle of 144(3)° (e.s.d. in parentheses; ref. 20). The ^{13}C NMR chemical shift of 211.4 p.p.m. for $[\kappa^2\text{-}C_2\text{-}C_6H_3Me(NC)_2]W(PMe_3)_4$ (see Supplementary Information) is thus also consistent with considerable backbonding in this molecule.

An interesting point to note is that chelating isocyanide ligands are not common because M–C–N–R moieties prefer to adopt linear coordination at both nitrogen and carbon[21]. For this reason, although $o\text{-}(CN)_2C_6H_4$ has been employed as a ligand, it does not chelate but instead serves as a bridging ligand[22]. In accord with such behaviour, the smallest ring size previously reported for a complex of a bidentate di(isocyanide) ligand is 12, as illustrated by $[\kappa^2\text{-}C_2\text{-}CH_2\{OC_6H_4(NC)\}_2]Cr(CO)_4$ (ref. 23). The 7-membered ring of $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$, featuring two W–C–N bond angles that are close to linear (165°–169°), is thus exceptionally small for a transition-metal complex of a bidentate di(isocyanide) ligand. The ability to isolate such an unusual compound may result from the fact that its mechanism of formation involves insertion of the tungsten centre into the aromatic ring; indeed, treatment of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with $o\text{-}(CN)_2C_6H_4$ at room temperature results in the immediate formation of an unidentified precipitate, with no evidence for formation of $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$ by ^1H NMR spectroscopy.

Several different mechanisms could explain the observed formation of $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$, of which one involves the direct insertion of tungsten into the C–C bond followed by two α-hydrogen elimination steps. Such a process is in line with the observation that electron-donating substituents on olefins promote C–C bond cleavage, as exemplified by the use of enetetramines to generate *N*-heterocyclic carbene compounds[24,25]. However, we favour the alternative mechanism outlined in Fig. 4 that comprises a series of C–H bond cleavage reactions to access a benzyne-type intermediate $[\eta^2\text{-}C_2\text{-}C_6H_4(NCCN)]W(PMe_3)_4H_2$, from which $[\kappa^2\text{-}C_2\text{-}C_6H_4(NC)_2]W(PMe_3)_4$ is then obtained via a sequence that involves reductive elimination of H_2 and C–C bond cleavage. The feasibility of this mechanism is supported by the report of the ruthenium benzyne

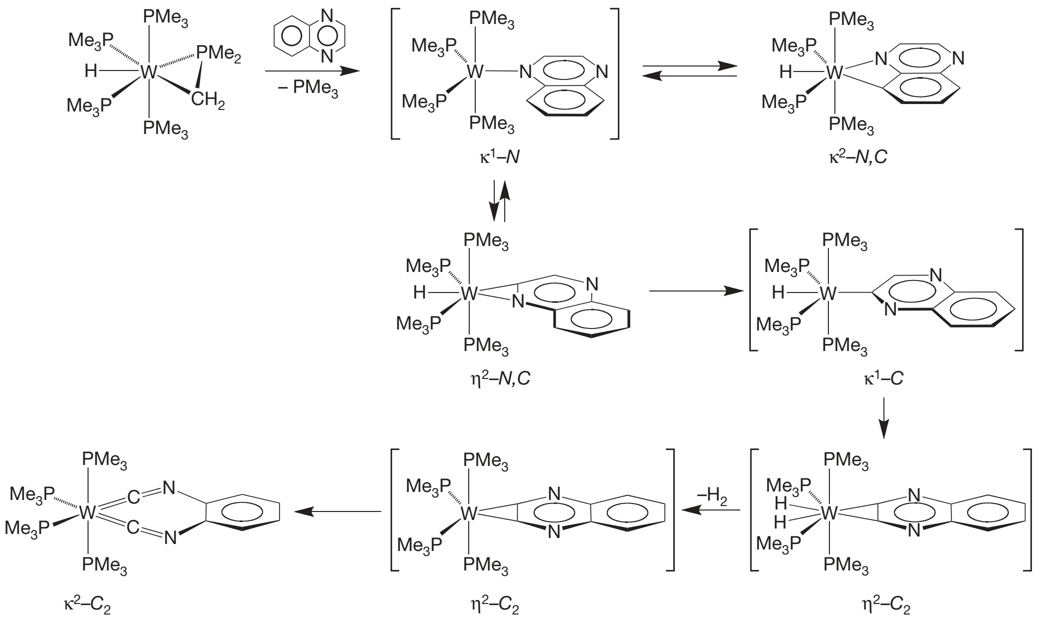

Figure 4 | Possible mechanism for formation of [κ^2-C_2-$C_6H_4(NC)_2$]$W(PMe_3)_4$.

complex (η^2-C_6H_4)$Ru(PMe_3)_4$ (ref. 26), a structural analogue of the proposed intermediate [η^2-C_2-$C_6H_4(NCCN)_2$]$W(PMe_3)_4$. Furthermore, the observation of several other compounds such as mononuclear (η^2-*N*,*C*-Qox)$W(PMe_3)_4H$ and (κ^2-*N*,*C*-Qox)$W(PMe_3)_4H$ (Fig. 4), and dinuclear (μ–η^2-*N*,*C*-κ^2-*N*,*C*-Qox′)[$W(PMe_3)_4H]_2$ (Supplementary Fig. 2), during the course of the reaction provides evidence that C–H bond cleavage is facile in this system. Note, however, that C–H bond cleavage is reversible and that the mere observation of (η^2-*N*,*C*-Qox)$W(PMe_3)_4H$ is thus not proof that this species is directly involved in the C–C bond cleavage process. A computational analysis of the reaction is, therefore, needed to establish which of the different mechanisms is the most reasonable for the observed transformations.

Finally, we note that the overall cleavage of the C–C bond of the benzyne-type species proposed in this system resembles the formation of *bis*(isocyanide) compounds by base-induced cleavage of diaminoacetylene species[27], a process that is the reverse of the well-known coupling reactions of isocyanides[25,28,29]. It is also worth noting that acetylenic C–C bonds have been successfully cleaved using metal-cluster complexes[30].

In conclusion, we note that the cleavage of an aromatic C–C bond by insertion of tungsten into an aromatic ring enables a quinoxaline compound to be converted to an *o*-diisocyanobenzene derivative, a transformation that may potentially be extended to other systems and thereby provide a new means of functionalizing aromatic molecules.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions G.P. supervised the project. A.S. synthesized and characterized the compounds. G.P. and A.S. analysed the data and wrote the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Database (CCDC #734113–734121). Correspondence and requests for materials should be addressed to G.P. (parkin@columbia.edu).