Dihydrobis(pyrazolyl)borate Alkylidyne Complexes of Tungsten[‡]

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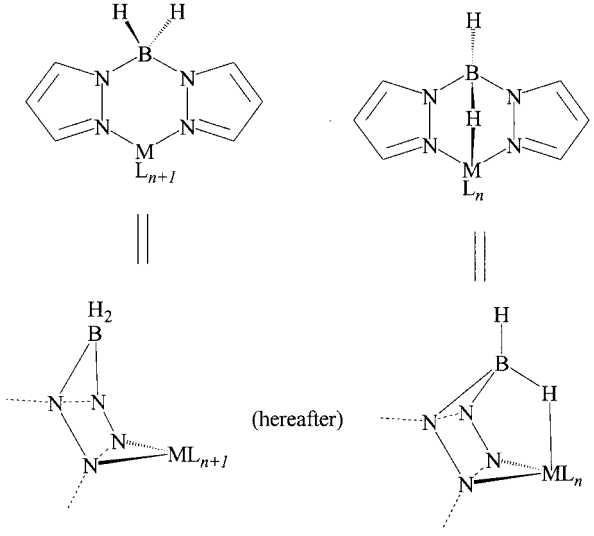
$[W(\equiv CR)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (R = $C_6H_3Me_2$-2,6 **1a**, $C_6H_2Me_3$-2,4,6 **1b**) react with $K[H_2B(pz)_2]$ (pz = pyrazol-1-yl) to provide two interconverting isomers of $[W(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (**2**), one isomer having been structurally characterised for R = $C_6H_3Me_2$-2,6 (**2a**). The reactions of $[W(\equiv CR)Br(CO)_2(CNR')_2]$ (**5**: R′ = $C_6H_3Me_2$-2,6, $CNMe_3$) with $K[H_2B(pz)_2]$ or of $[W(\equiv CR)Br(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (**2**) with isocyanides are more complex due to the facile formation of unstable ketenyl derivatives. In the absence of light, the reaction of $[W(\equiv CR)Br(CO)_2(CNR')_2]$ (**5**) with $K[H_2B(pz)_2]$ provides $[W(\equiv CR)(CO)_2(CNR')\{H_2B(pz)_2\}]$ (**3**) in moderate yield, similar yields were obtained from $[W(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (**2**) and CNR′. Under mild photolytic conditions both combinations provide primarily the thermally unstable ketenyl complex $[W(\eta^2\text{-}OCCR)(CO)(CNR')_2\{H_2B(pz)_2\}]$ (**4**). The picoline ligand in $[W(\equiv CR)Br(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (**2**) is readily replaced by PMe_2Ph to provide $[W(\equiv CR)(CO)_2(PMe_2Ph)\{H_2B(pz)_2\}]$ (structurally characterised for R = $C_6H_3Me_2$-2,6 **6a**). The reaction of either $[W(\equiv CR)(CO)_2(PMe_2Ph)\{H_2B(pz)_2\}]$ (**6**) or $[W(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (R = $C_6H_2Me_3$-2,4,6 **2b**) with excess PMe_2Ph provides $[W(\equiv CR)(CO)(PMe_2Ph)_2\{H_2B(pz)_2\}]$ (**7**). This complex is also obtained from $K[H_2B(pz)_2]$ and $[W(\equiv CR)Br(CO)(PMe_2Ph)_3]$ (**8**), the latter arising from the reaction of $[W(\equiv CR)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (**1b**) with PMe_2Ph.

Introduction

The chemistry of alkylidyne complexes of tungsten[2] has been greatly enriched by use of hydrotris(pyrazolyl)borate ligands and their derivatives,[3] primarily from the works of Stone,[4] Angelici,[5] and Templeton.[6] The dihydrobis(pyrazolyl)borate chelate $[H_2B(pz)_2$; pz = pyrazol-1-yl; Scheme 1][3] is an intriguing ligand in its own right displaying a propensity for η^3-coordination through agostic and potentially hemilabile B−H−M interactions.

In the design of alkylidyne complexes for use in both stoichiometric and catalytic bond-forming processes, the incorporation of a vacant coordination site *cis* to the alkylidyne ligand remains a valuable goal, although this can present a challenge for low-valent metal centres which are typically more constrained by adherence to the 18-electron rule. Stone has described a range of tungsten alkylidyne complexes coligated by the $H_2B(pz)_2$ ligand and shown that they readily enter into bridge-assisted cluster-assembly reactions (Scheme 2).[7] The further observation that $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)\{P(OMe)_3\}_2\{H_2B(pz)_2\}]$ reacts stoichiometrically with $P\equiv CCMe_3$ under mild conditions



Scheme 1. Dihydrobis(pyrazolyl)borate coordination

to provide $[Mo(\equiv CCMe_3)(CO)\{P(OMe)_3\}_2\{H_2B(pz)_2\}]$[8] points toward the intermediacy of coordinatively unsaturated species, if an analogy with alkyne metathesis is entertained. However, no direct observation of the operation of the η^3-coordination mode was ever made in these processes. We considered that the $H_2B(pz)_2$ ligand might nevertheless, under suitably contrived circumstances, enter into η^3-coordination and thereby satisfy the above requirements by virtue of the hemilability of the agostic B−H−M interaction.

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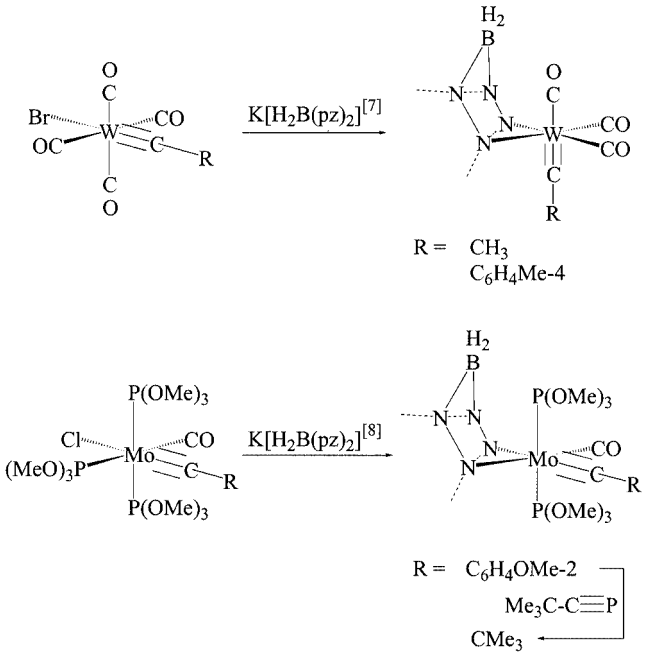


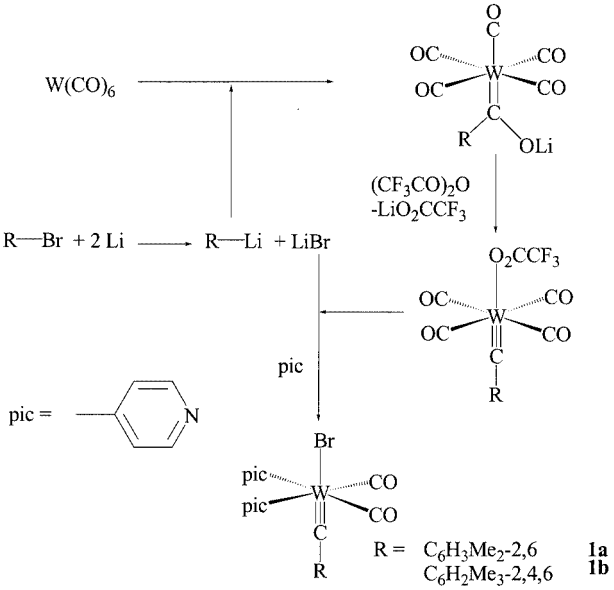
Scheme 2. Dihydrobis(pyrazolyl)borate alkylidynes[7,8]

The results described herein arise from an attempt to broaden the class of alkylidyne-$H_2B(pz)_2$ complexes in pursuit of such a situation. Although coordination of the $H_2B(pz)_2$ ligand has been structurally confirmed in the chemistry of chromium,[9] the Cambridge Crystallographic Data Centre contains no data for mononuclear $H_2B(pz)_2$ complexes of either molybdenum[10] or tungsten and accordingly, two crystallographic studies of complexes with the $H_2B(pz)_2W$ motif were undertaken.

Results and Discussion

Stone's original approach to alkylidyne complexes coligated by the $H_2B(pz)_2$ ligand, namely $[W(\equiv CR)(CO)_3\{\kappa^2\text{-}H_2B(pz)_2\}]$ (R = Me, C_6H_4Me-4; hereafter κ^2 implied unless otherwise indicated),[7] proceeded from Fischer's thermolabile precursors *trans*-$[W(\equiv CR)Br(CO)_4]$. Whilst the instability of the tetracarbonyl precursors did not preclude a detailed study of $[W(\equiv CR)(CO)_3\{H_2B(pz)_2\}]$, we sought a more convenient entry point. To this end, thermally stable bis(γ-picoline) precursor complexes were employed. We have previously employed the sterically congested xylylmethylidyne ligand to confer kinetic stability on alkylidyne complexes.[13] More recently, Berke employed the mesitylmethylidyne variant and this allowed the observation of rare examples of hydrido-alkylidyne complexes.[14]

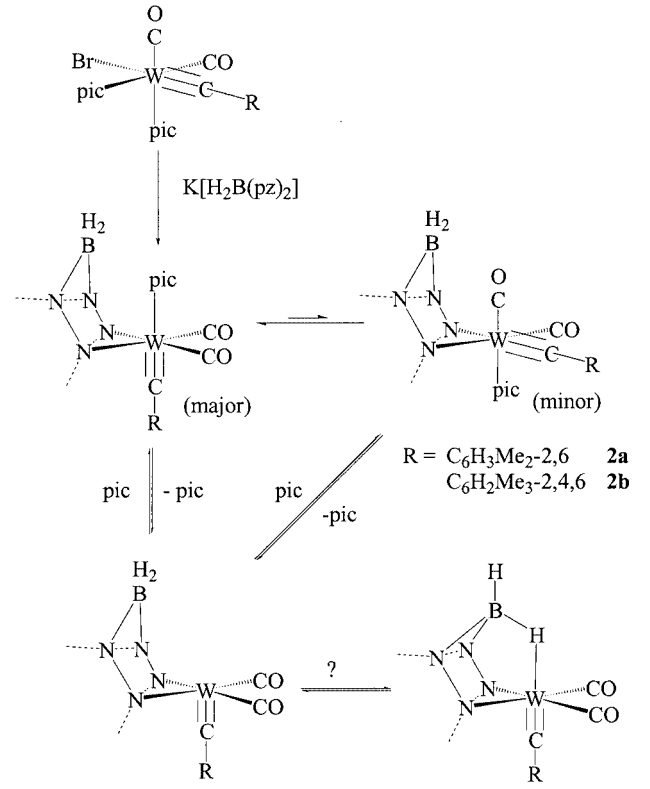
The complexes *trans,cis,cis*-$[W(\equiv CR)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (R = $C_6H_3Me_2$-2,6 **1a**, $C_6H_2Me_3$-2,4,6 **1b**) were readily obtained directly from $[W(CO)_6]$ in "one-pot" reactions by successive treatment with LiBr/LiR (from Li and RBr), $(CF_3CO)_2O$ and γ-picoline (Scheme 3), following a modification/combination of Mayr's syntheses of $[W(\equiv CPh)Cl(CO)_2(NC_5H_4)_2]$ and $[W(\equiv CPh)(O_2CCF_3)(CO)_2(tmeda)]$.[15,16] The 2-xylyl derivative **1a** has been previously employed for the preparation of various "half-sandwich" alkylidyne complexes, although its synthesis was not described.[13] The chloro(pyridine)mesitylmethylidyne complex $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Cl(CO)_2(NC_5H_5)_2]$ has recently been reported[14] by the Mayr synthesis from the reaction of Fischer's pre-isolated aroylate salt $[W\{C(=O)C_6H_2Me_3\text{-}2,4,6\}(CO)_5][NMe_4]$[17] with oxalyl chloride and pyridine. Whilst this salt would presumably also serve as a precursor for the subsequent introduction of the $H_2B(pz)_2$ ligand, the present high yielding "one-pot" synthesis of $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (**1a**) is both more convenient and atom efficient in a "green" sense. Specifically, by omitting the Li/NMe_4 metathesis step in the original Mayr synthesis, the bromide anion carried through from the original synthesis of the aryllithium replaces the trifluoroactetate ligand in the intermediate $[W(\equiv CR)(O_2CCF_3)(CO)_4]$. γ-Picoline was chosen to simplify the NMR data. Spectroscopic data for the complexes are unremarkable and conform to precedent.[2]



Scheme 3. One Pot Synthesis of alkylidyne tungsten precursors

The reactions of **1a** or **1b** with $K[H_2B(pz)_2]$ in propanone or dichloromethane provide high yields of the complexes formulated as $[W(\equiv CR)(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]$ (R = $C_6H_3Me_2$-2,6 **2a**, $C_6H_2Me_3$-2,4,6 **2b**) on the basis of spectroscopic data and a crystallographic study (vide infra) of **2a**. Infrared (solution and solid-state) and ^1H NMR spectroscopic data for both **2a** and **2b** would appear to suggest the formation of one isomer, however, in this instance $^{13}C\{^1H\}$ NMR spectroscopic data appear more sensitive to the coordination environment around tungsten, revealing the coexistence of two isomers in solution (Scheme 4). Thus for **2b**, two carbyne associated resonances are observed at low field [δ = 294.5 (major), 284.5 (minor) ppm]. Similarly, the carbonyl resonances are observed in similar ratios; however, these latter data also allow the assignment of the

stereochemistry at tungsten. Thus, the major isomer has only one carbonyl environment (δ = 225.3 ppm) whilst the minor isomer features two carbonyl resonances (δ = 227.5 and 221.5 ppm). Accordingly, the major isomer corresponds to the more symmetric geometry (i.e. with the picoline ligand *trans* to the alkylidyne substituent) which is also found in the solid state (Scheme 4, Figure 1). Similar behaviour was observed for **2b**.



Scheme 4

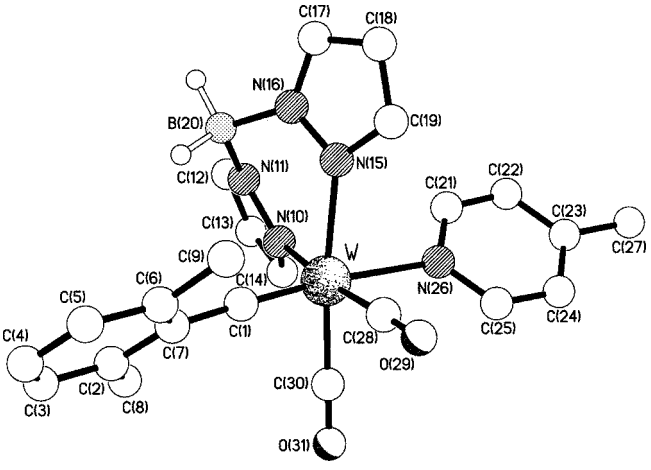


Figure 1. Molecular geometry of **2a**; hydrocarbon hydrogen atoms omitted

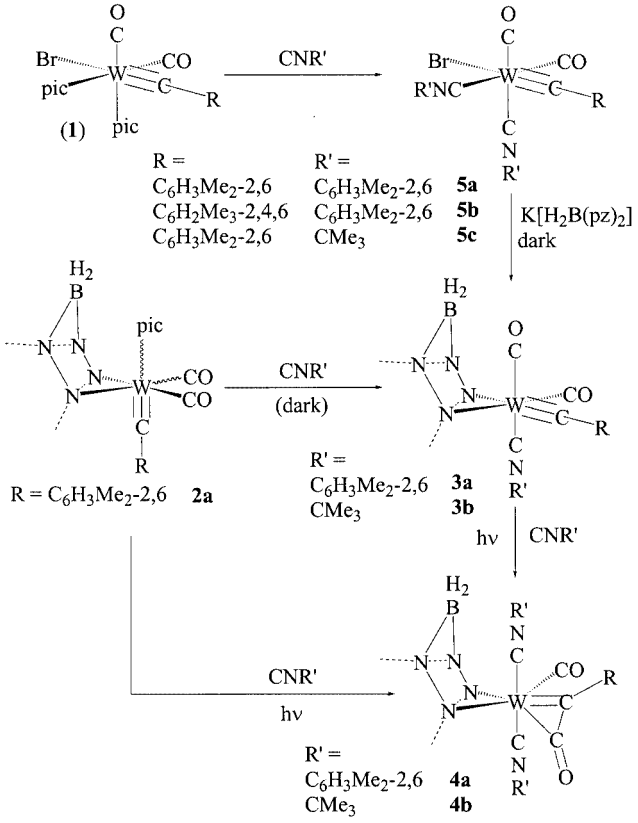
For both isomers to coexist and interconvert in solution, it may be surmised that the donor properties of the pyrazole and picoline groups are comparable. Since this equilibrium operates under mild conditions, it seems most likely that it occurs through dissociation of the picoline ligand, rearrangement of the five-coordinate complex and picoline recoordination, rather than unimolecular rearrangement of the octahedral complexes. The lability of the picoline ligand in **2** is also implicit in the ligand-substitution reactions discussed below. It might also be inferred that if tridentate coordination of the $H_2B(pz)_2$ ligand occurs to stabilize the five-coordinate intermediate, then this is easily replaced by picoline coordination since no spectroscopic evidence was obtained for such an intermediate.

The reactions of **2** with a range of ligands were investigated. Under ambient conditions neither **2a** nor **2b** appear to react with carbon monoxide within spectroscopically (IR) determinable limits. This is in contrast to the complex $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)\{P(OMe)_3\}_2\{H_2B(pz)_2\}]$[8] which equilibrates to a mixture with the complex $[Mo(\equiv CC_6H_4OMe\text{-}2)(CO)_2\{P(OMe)_3\}\{H_2B(pz)_2\}]$ under one atmosphere of CO in dichloromethane.[18] However, it is not surprising given that introduction of a further carbonyl ligand would be disfavored by the competitive π-acidity of the two carbonyl and alkylidyne ligands already present. The complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_3\{H_2B(pz)_2\}]$[7] has already been discussed (see above) and the synthesis proceeds in the absence of other potential donor ligands.

Isonitriles (CNR′: R′ = CMe_3, $C_6H_3Me_2$-2,6) which are more nucleophilic and less π-acidic ligands than CO do react with **2** by displacement of the picoline ligand. However, these reactions are complicated by the competitive formation of the ketenyl species. Thus, treating **2a** with either $CNCMe_3$ or $CNC_6H_3Me_2$-2,6 leads to complex mixtures. This was eventually traced to the competition of thermal and photochemical processes, each leading to thermally sensitive products. The major identifiable products of the thermal reaction were the alkylidyne complexes $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(CNR')\{H_2B(pz)_2\}]$ (**3**), whilst the major photo-products were the ketenyl complexes $[W(\eta^2\text{-}OCC_6H_3Me_2\text{-}2,6)(CO)(CNR')_2\{H_2B(pz)_2\}]$ (R′ = $C_6H_3Me_2$-2,6 **4a**, CMe_3 **4b**).

Kreiβl[19] studied the coupling of alkylidyne and carbonyl ligands to generate mononuclear ketenyl complexes in thermal reactions of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with PMe_3, whilst Stone showed similar couplings in dinuclear systems.[20] Subsequently, Geoffroy demonstrated that such processes could be photochemically induced.[21] Ketenyl formation through alkylidyne/carbonyl coupling has since been reviewed,[22] whilst the synthetic utility of ketenyl complexes has been amply demonstrated by Kreiβl.[23] The clarification of the processes involved in the reactions of **2** with isocyanides called for selective synthesis of the products since the reactions themselves were not synthetically useful in that the mixtures obtained required cryostatic chromatography (−40 °C) and the purified products were unstable at room temperature. The purple ketenyl complex $[W(\eta^2\text{-}OCC_6H_3Me_2\text{-}2,6)(CO)(CNCMe_3)_2\{H_2B(pz)_2\}]$ (**4b**) could most easily be obtained in modest yield (40 %) by the addition of $CNCMe_3$ to **2a** under irradiation (domestic sun

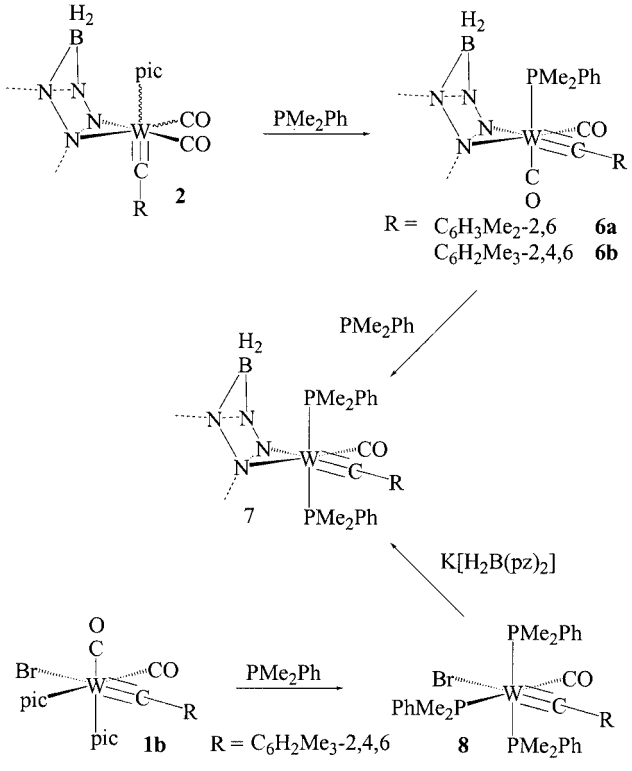
lamp) followed by cryostatic chromatography. Although they could be retrospectively identified amongst the products of the reactions of **2** with CNR′, the alkylidyne complexes $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(CNR')\{H_2B(pz)_2\}]$ (R′ = $C_6H_3Me_2$-2,6 **3a**, CMe_3 **3b**) could most easily be obtained through the reactions of preformed $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(CNR')_2]$ (R′ = CMe_3 **5a**, $C_6H_3Me_2$-2,6 **5b**; Scheme 5)[24] with $K[H_2B(pz)_2]$, although exclusion of light was essential throughout their synthesis and isolation.



Scheme 5

The formulation of both the alkylidyne and ketenyl complexes rests upon spectroscopic and FAB-MS data, since their instability at ambient temperatures prevented us from obtaining either satisfactory elemental microanalysis or crystallographic grade crystals. Nevertheless, the spectroscopic data strongly support the formulations as do the unequivocal synthesis from bis(isocyanide) precursors. For the alkylidyne complex $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(CNCMe_3)\{H_2B(pz)_2\}]$ (**3b**), both ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data confirm two distinct pyrazolyl environments, the latter also indicating chemically inequivalent carbonyl ligands. Taken together, these data are only consistent with the geometry shown in Scheme 5. Such arguments also support a similar geometry for **3a**. For the ketenyl complex $[W(\eta^2\text{-}OCCC_6H_3Me_2\text{-}2,6)(CO)(CNCMe_3)_2\{H_2B(pz)_2\}]$ (**4b**) the stereochemistry at tungsten also follows from a combination of IR and NMR spectroscopic data, the gross formulation being confirmed by FAB-MS data. Thus one isocyanide-associated absorption is observed in the infrared spectrum and one albeit broad resonance in the $^{13}C\{^1H\}$ NMR spectrum indicating a *trans*-$W(CNCMe_3)_2$ arrangement. The observation of a single isocyanide environment would suggest that either inversion of the $B(NN)_2W$ boat arrangement is rapid on the NMR timescale or that the BH_2 group does not sufficiently closely approach the *tert*-butyl groups to render these inequivalent. Molecular models and the related structural studies (vide infra) would argue for the former interpretation.

In contrast to the reactions with isocyanides, the reactions of **2** with dimethylphenylphosphane are straightforward and proceed through picoline substitution to provide a single isomer with no indication of ketenyl formation. Thus, treating **2** with one equivalent of PMe_2Ph in dichloromethane provided the complexes $[W(\equiv CR)(CO)_2(PMe_2Ph)\{H_2B(pz)_2\}]$ (R = $C_6H_3Me_2$-2,6 **6a**, $C_6H_2Me_3$-2,4,6 **6b**) each in only one isomeric form. The complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_3\{H_2B(pz)_2\}]$ has been reported to react with PPh_3 or PMe_3 to provide the complexes $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(PR_3)\{H_2B(pz)_2\}]$ by carbonyl substitution with no evidence for ketenyl formation.[7] The stereochemistry of **6a** in solution (Scheme 6, Figure 2) follows unequivocally from spectroscopic data and was confirmed by X-ray crystallography (vide infra). The diastereotopicity of the phosphane methyl groups confirms the absence of a molecular element of symmetry excluding the isomer with phosphane *trans* to the alkylidyne group. This possibility may also be discounted by the low value of $^2J_{P\text{-}C}$ (8.9 Hz) for the alkylidyne ^{13}C resonance. IR data



Scheme 6

indicates a *cis*-$W(CO)_2$ arrangement whilst ^{13}C NMR spectroscopic data indicate that both the CO ligands and also the two pyrazolyl groups are chemically inequivalent. Similar arguments apply to the stereochemistry of **6b**.

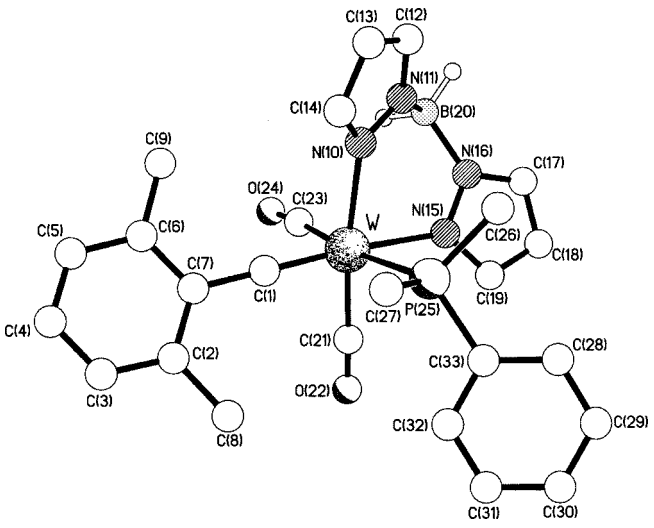


Figure 2. Molecular geometry of **6a**; hydrocarbon hydrogen atoms omitted

Treating the complex **6b** with excess PMe_2Ph leads to carbonyl substitution and formation of the *trans*-bis(phosphane) complex $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)(PMe_2Ph)_2\{H_2B(pz)_2\}]$ (**7**). The stereochemistry at tungsten follows from ^1H, ^{31}P and ^{13}C NMR spectroscopic data. The chemical equivalence of the two phosphorus nuclei is manifest as a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum, whilst the *trans* arrangement is suggested by the virtual triplet nature of the ^{13}C resonance for the phosphane methyl groups. Notably this stereochemistry is equivalent to that proposed for $[Mo(\equiv CR)(CO)\{P(OMe)_3\}_2\{H_2B(pz)_2\}]$ (R = CMe_3, C_6H_4OMe-2).[8] The IR data [ν(CO) = 1992, 1903 cm^{-1}] for **6b** would suggest that the carbonyl ligands are not thermally labile. Accordingly, the facile formation of **7** from **6b** under mild conditions presumably proceeds through ketenyl formation followed by CO extrusion, as has been demonstrated in the synthesis of $[W(C\equiv CC_6H_4Me\text{-}4)(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ from $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.[19] Notably, the reactions of $[W(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (R = C_6H_4Me-4, SMe) with PMe_3 or PEt_3 stop at the ketenyl stage providing $[W(\eta^2\text{-}OCCC_6H_4Me\text{-}4)(CO)(PMe_3)\{HB(pz)_3\}]$[7] and $[W(\eta^2\text{-}OCCSMe)(CO)(PEt_3)\{HB(pz)_3\}]$,[5a] respectively.

An alternative synthesis of **7** was developed by the reaction of $[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)(PMe_2Ph)_3]$ (**8**) with $K[H_2B(pz)_2]$. The new precursor **8** was obtained from the reaction of **1b** with PMe_2Ph. The closely related complex $[W(\equiv CPh)Cl(CO)(PMe_3)_3]$ has been reported previously by Mayr, arising from the reaction of $[W(\equiv CPh)Cl(CO)_2(PMe_3)_2]$ with PMe_3 over a period of 7 days.[27] In the present case however the stoichiometric amount of phosphane suffices and the reaction is complete in 15 h. The *mer* geometry follows from ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopic data for the phosphane groups and the doublet-triplet fine structure of the carbonyl and alkylidyne group resonances in the $^{13}C\{^1H\}$ NMR spectrum. The complex **8** reacts cleanly with $K[H_2B(pz)_2]$ in tetrahydrofuran to provide **7**. In this case it is not necessary to invoke ketenyl intermediates.

Crystal Structure of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(NC_5H_4Me\text{-}4)\{H_2B(pz)_2\}]\cdot 0.5CH_2Cl_2$ (2a·0.5CH_2Cl_2)

The complex crystallizes from a mixture of dichloromethane and petroleum ether as a dichloromethane hemisolvate, however, the solvent of crystallization which is disordered shows no directional interactions with the complex and neither are there any notable intermolecular interactions within the crystal lattice. The molecular geometry of the complex is depicted in Figure 1 and selected bond lengths and angles are presented in Table 1. The geometry at tungsten is distorted octahedral with angles between adjacent ligands lying in the range 82.9(2)−101.2(2)° such that the pyrazolyl groups bend away from the alkylidyne groups [C(1)−W−N(15) 100.5(2), C(1)−W−N(10) 101.2(2)°] whilst the carbonyl ligands bend less markedly towards it [C(1)−W−C(28) 85.6(3), C(1)−W−C(30) 87.9(3)°]. The bending of *cis* ligands away from metal−element multiple bonds is not uncommon and it has been suggested that this strengthens the multiple bonding.[28] The alkylidyne ligand is essentially linear at the carbyne carbon [W−C(1)−C(7) 178.0(5)°] and the W≡C separation of 1.810(6) Å falls within the range typical of alkylidyne tungsten complexes[2] and is similar to that found in, for example, $[W(\equiv CPh)(CO)_2(Ppy_3)]^+$ [1.811(7) Å].[29] The xylyl ring orientation is presumably dictated by steric effects as it places the *ortho* substituents between adjacent coligands, rather than allowing the aromatic π-system to conjugate with occupied metal t_{2g} orbitals. In a similar manner, the plane of the picoline ligand is approximately orthogonal (ca. 79°) to that of the alkylidyne, lying between the pyrazolyl rings of the $H_2B(pz)_2$ chelate and approximately bisecting the $W(CO)_2$ group. The octahedral γ-picoline complexes *trans*-$[W^{III}Cl_4(NC_5H_4Me\text{-}4)_2]^-$,[30] *cis,cis,trans*-$[W^{II}Br_2(bipy)(NC_5H_4Me\text{-}4)_2]$[31] and $[W^0(CO)_5(NC_5H_4Me\text{-}4)]$[32] have (mean) W−N bond lengths of 2.166, 2.176, and 2.257 Å, respectively, with a lengthening of the W−N bond on reduction of the metal centre (W^{III}, W^{II}, and W^0). For-

Table 1. Selected bond lengths (Å) and angles (°) for **2a**

W−C(1)	1.810(6)	W−C(28)	1.975(8)
W−C(30)	1.977(9)	W−N(15)	2.201(6)
W−N(10)	2.204(6)	W−N(26)	2.378(5)
C(1)−C(7)	1.416(9)		
C(1)−W−C(28)	85.6(3)	C(1)−W−C(30)	87.9(3)
C(28)−W−C(30)	87.6(3)	C(1)−W−N(15)	100.5(2)
C(28)−W−N(15)	94.3(3)	C(30)−W−N(15)	171.5(2)
C(1)−W−N(10)	101.2(2)	C(28)−W−N(10)	173.1(3)
C(30)−W−N(10)	93.6(3)	N(15)−W−N(10)	83.6(2)
C(1)−W−N(26)	173.8(2)	C(28)−W−N(26)	88.9(3)
C(30)−W−N(26)	88.9(2)	N(15)−W−N(26)	82.88(19)
N(10)−W−N(26)	84.30(18)	C(7)−C(1)−W	178.0(5)

mal oxidation states have little meaning in compounds with metal−carbon multiple bonding. However, the sensitivity of the W−N bond lengths to the π-acidity of *trans*-disposed ligands has been demonstrated for the bis(pyridine) complex [W(≡CPh)Cl(CO)(ma)(py)$_2$][33] where the W−N bond *trans* to the strongly π-acidic maleic anhydride (ma) is longer (2.253 Å) than that *trans* to CO (2.233 Å). The W−N(26) bond length of 2.378(5) Å seen here for **2a** far exceeds those discussed above and is consistent with the lability demonstrated in reactions with CNR′ and PMe_2Ph and also its facile isomerism. This lengthening is also consistent with its location *trans* to an alkylidyne ligand which is generally considered to be strongest of all carbon π-acid ligands.

The W(pz)$_2$BH$_2$ metallacycle adopts a typical boat formation with both the tungsten and boron atoms lying ca. 0.65 Å out of the plane of the four nitrogen atoms which are coplanar to within 0.007 Å. This geometry is comparatively shallow and positions the BH_2 group well beyond any interaction with either the metal [BH···W 3.46 Å] or co-ligands. Thus, although the adopted conformation places the BH_2 adjacent to the alkylidyne, the BH···C(1) distance of 3.10 Å is probably too long to invoke any incipient nucleophilic interaction of the B−H bond with the carbyne carbon atom. The bite of the chelate at 83.6(2)° is somewhat contracted from 90° with the remaining angles within the chelate close to those expected for trigonal nitrogen [121.7(6)−125.0(4)°] and tetrahedral boron [107.9(6)°].

Crystal Structure of [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(PMe$_2$Ph){H$_2$B(pz)$_2$}] (6a)

Yellow solvate-free needles were obtained by cooling a solution of the complex in a mixture of propanone and petroleum ether (40:60). The molecular geometry of the complex is depicted in Figure 2. As for complex **2a**, the tungsten center approximates octahedral geometry with angles between *cis*-ligands falling in the range 81.70(8)−100.00(11)° (Table 2). However, in contrast to **2a**, the $H_2B(pz)_2$ and alkylidyne groups assume a meridional disposition with the phosphane ligand *cis* to the alkylidyne group. The alkylidyne ligand displays a characteristically short W≡C separation [1.825(4) Å] (not significantly different from that in **2a**) and is slightly bent at the carbyne carbon atom [W−C(1)−C(7) 173.5(3)°], which lies within the range previously observed and generally attributed to crystal-packing effects.[2] The orientation of the xylyl group is such as to minimise steric interactions with *cis* coligands, which places the *ortho* substituents either side of the $W(CO)_2$ unit. The phosphane ligand has a W−P bond length of 2.564(1) Å which appears somewhat long. Limiting comparison to 6-coordinate tungsten complexes of PMe_2Ph with sterically modest co-ligands[34,35] there appears to be no obvious correlation between the oxidation state (d configuration) and the W−P bond length [d^6: 2.480−2.524; d^4: 2.484−2.512; d^3: 2.513−2.561; d^2: 2.481−2.538Å]. The dichotomy that clouds the assignment of oxidation states for alkylidyne complexes is shared by nitrosyl ligands and accordingly the most suitable structure for comparison is the complex *trans,cis,cis*-[W(NO)I(CO)$_2$(PMe$_2$Ph)$_2$] reported by Basolo[35] which also features particularly long W−P bond lengths [2.582(2), 2.554(2) Å].

The [H$_2$B(NN)$_2$W] chelate once again adopts a shallow boat conformation with here the tungsten and boron atoms that lie (0.54 and 0.65 Å, respectively) out of the N_4 plane which is coplanar to within 0.026 Å. The closest B−H hydrogen atom approach to the metal centre is 3.49 Å, too distant for any interaction. However, this hydrogen atom is positioned directly above one of the carbonyl ligands, the BH···C(23) distance being 2.87 Å, indicating a possible weak B−H···π* interaction. In contrast to **2a**, the low symmetry of **6a** allows the chelate to reveal the comparative *trans* influences of carbonyl and alkylidyne ligands. Thus the pyrazolyl group *trans* to the alkylidyne has a significantly (20σ) longer W−N bond length [2.292(3) Å] than that *trans* to the carbonyl [2.233(3) Å]. The difference in *trans* influence for the pyrazolyl and phosphane ligands is less obvious in the bonding of the carbonyl ligands with that *trans* to phosphorus [W−C(23) 2.014(5) Å], showing a smaller (7σ) lengthening relative to W−C(21) [1.980(4) Å]. The only intermolecular packing interaction of note is a parallel π−π stacking of the xylyl rings of centrosymmetrically related molecules with mean interplanar and centroid···centroid separations of 3.46 and 3.74 Å, respectively.

Table 2. Selected bond lengths (Å) and angles (°) for **6a**

W−C(1)	1.825(4)	W−C(21)	1.980(4)
W−C(23)	2.014(5)	W−N(10)	2.233(3)
W−N(15)	2.292(3)	W−P(25)	2.5644(10)
C(1)−C(7)	1.451(5)		
C(1)−W−C(21)	87.74(15)	C(1)−W−C(23)	86.64(16)
C(21)−W−C(23)	87.66(17)	C(1)−W−N(10)	99.92(13)
C(21)−W−N(10)	172.25(13)	C(23)−W−N(10)	93.91(14)
C(1)−W−N(15)	174.94(13)	C(21)−W−N(15)	87.35(14)
C(23)−W−N(15)	91.95(15)	N(10)−W−N(15)	85.02(11)
C(1)−W−P(25)	100.00(11)	C(21)−W−P(25)	95.61(12)
C(23)−W−P(25)	172.69(12)	N(10)−W−P(25)	82.00(8)
N(15)−W−P(25)	81.70(8)	C(7)−C(1)−W	173.5(3)

Experimental Section

General Procedures: All manipulations were carried out under an atmosphere of prepurified dinitrogen with conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent [ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH_2]. Light petroleum ether refers to that fraction of boiling point 40−60 °C. Chromatographic separations were routinely performed using a cryostatically cooled column at −40 °C. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded with a Jeol JNM EX270 NMR spectrometer and referenced against internal Me_4Si (^{1}H), internal $CDCl_3$ (^{13}C) or external H_3PO_4 (^{31}P). Infrared spectra were recorded with a Perkin−Elmer 1720-X FT-IR spectrometer. FAB-Mass spectra were measured with an Autospec Q mass spectrometer using 3-nitrobenzyl alcohol as matrix ('pic' = γ-picoline). Photolyses were conducted with a domestic sun-lamp in cryo-

statically cooled Schlenk-tubes. Commercial reagents were used as received and the salt $K[H_2B(pz)_2]$[3] prepared according to the following procedure. The original procedure involves heating $K[BH_4]$ and Hpz in a melt, with the progress of the reaction being monitored by the measurement of evolved hydrogen gas. In our laboratory, this usually provided samples of $K[H_2B(pz)_2]$ contaminated with both pyrazole and $K[HB(pz)_3]$. The following approach employs a solvent to moderate the reaction temperature and provide a homogeneous reaction mixture.

Synthesis of Potassium Dihydrobis(pyrazolyl)borate: Potassium tetrahydroborate (13.50 g, 0.25 mmol) and pyrazole (68.00 g, 1.00 mol), both finely ground, were suspended in toluene (250 mL) and gradually brought to reflux. After 12−16 h hydrogen gas evolution had effectively ceased. The clear solution was filtered whilst hot to remove any residual traces of unchanged $K[BH_4]$. The filtrate was allowed to cool with rapid stirring to about 40 °C whereupon a white precipitate formed that was filtered off. The finely divided white solid was washed with dichloromethane (3 × 50 mL), to remove any traces of unchanged pyrazole followed by diethyl ether (2 × 30 mL) and then dried in vacuo. Yield 32.60 g (70 % vs. $K[BH_4]$). The salt was characterised by comparison of spectroscopic data with those previously reported[3] and was found to be free of Hpz or $K[HB(pz)_3]$ within spectroscopically determinable limits (^{1}H NMR, IR).

Synthesis of $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (1a): This complex has been used previously for the preparation of various 2-xylyl methylidyne complexes, however, neither preparative details nor spectroscopic data were provided.[13a] Tungsten hexacarbonyl (4.25 g, 12 mmol) was suspended in diethyl ether (30 mL) to which 1.1 equivalents of $LiC_6H_3Me_2$-2,6·LiBr in 1 mL aliquots over 30 min were subsequently added. The pale yellow solution was cooled (dry ice/propanone) and trifluoroacetic anhydride (1.70 mL, 12.0 mmol) slowly added over a 5 min period. The mixture was stirred for 15 min after which γ-picoline (3.0 mL, 0.957 gcm^{-3}, 30 mmol) was added and allowed to warm to room temperature which resulted in evolution of carbon monoxide (CAUTION). After 12 h, a bright yellow precipitate was isolated from solution. This solid was redissolved in dichloromethane (20 mL) and the solution filtered under nitrogen through a plug of alumina (2 × 4 cm). The filtrate was diluted with diethyl ether (60 mL) and then cooled to −10 °C whereupon the bright orange solid which formed was isolated by filtration and dried in vacuo. Yield 6.38 g (85 %). IR (CH_2Cl_2): ν(CO) = 1984, 1895 cm^{-1}. Nujol: ν(CO) = 1980, 1888 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.40, 2.45 [s × 2, 6 H × 2, $C_6H_3CH_3$ and $NC_5H_4CH_3$], 6.90 [d, 2 H, H3,5 (C_6H_3)], 7.03 [m, 1 H, H4 (C_6H_3)], 7.11, 8.97 [$(AB)_4$, 8 H, NC_5H_4, ^3J(AB) = 5.5 Hz] ppm. ^{13}C{^{1}H} NMR: δ = 266.4 [W≡C, ^1J (WC) = 207 Hz], 221.9 [WCO, ^1J (WC) = 171 Hz], 150.5−127.2 [C_6H_3 and NC_5H_4], 125.8 [C-3,5 (NC_5H_4)], 21.0, 20.5 ($C_6H_4CH_3$ and $NC_5H_4CH_3$) ppm. FAB-MS: *m*/*z* = 624 [M]$^+$, 596 [M − CO]$^+$, 568 [M − 2CO]$^+$, 543 [M − Br]$^+$, 529 [M − pic]$^+$, 503 [M − pic − CO]$^+$, 473 [M − pic − 2CO]$^+$, 450 [M − pic − Br]$^+$. $C_{23}H_{23}BrN_2O_2W$: calcd. C 44.33, H 3.72, N 4.50; found C 44.8, H 3.5, N 4.4.

Synthesis of *trans,cis,cis*-$[W(\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (1b): The synthesis follows the procedure described above, providing 6.74 g (88 %) of the desired complex from $[W(CO)_6]$ (4.25 g, 12.0 mmol). IR (CH_2Cl_2): ν(CO) = 1984, 1895 cm^{-1}. IR (nujol): ν(CO) = 1980, 1888 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.20 [s, 3 H, $C_6H_2CH_3$-4], 2.40, 2.43 [s × 2, 12 H, $NC_5H_4CH_3$ and $C_6H_2CH_3$-2,6], 6.75 [s, 2 H, C_6H_2], 7.09, 8.95 [$(AB)_4$, 8 H, (NC_5H_4), ^3J(AB) = 5.6 Hz] ppm. ^{13}C{^{1}H} NMR: δ = 267.3 [W≡C, ^1J (WC) = 207.0 Hz], 222.2 [WCO, ^1J(WC) = 171.3 Hz], 153.2 [C-2,6 (NC_5H_4)], 150.6 [C-4 (NC_5H_4)], 143.8 [C-1 (C_6H_2)], 141.4 [C-2,6 (C_6H_2)], 137.7 [C-4(C_6H_2)], 128.1 [C-3,5 (C_6H_2)], 125.9 [C-3,5(NC_5H_4)], 21.4 ($C_6H_2CH_3$-4), 21.3, 20.6 ($NC_5H_4CH_3$ and $C_6H_2CH_3$-2,6) ppm. FAB-MS: *m*/*z* (%) = 638(29) [M]$^+$, 610(52) [M − CO]$^+$, 582(91) [M − 2CO]$^+$, 557(78) [M − Br]$^+$, 545(41) [M − pic]$^+$, 517(53) [M − pic-CO]$^+$, 487(63) [M − 2CO]$^+$, 464(37) [M − Br − pic]$^+$. $C_{24}H_{25}BrN_2O_2W$: calcd. C 45.24, H 3.95, N 4.40; found C 44.6, H 3.7, N 4.3.

Synthesis of *mer*- and *fac*-$[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(NC_5H_4\text{-}Me\text{-}4)\{H_2B(pz)_2\}]$ (2a): The salt $K[H_2B(pz)_2]$ (1.77 g, 9.50 mmol, 1.1 equiv.) was added to *trans,cis,cis*-$[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (**1a**, 5.00 g, 8.60 mmol) in propanone (30 mL) and the mixture was stirred for 12 h. The solution was concentrated in vacuo to about 10 mL and purified on an alumina-loaded column (2 × 30 cm) eluting with a mixture of propanone and hexane (1:2). The major orange fraction was collected, concentrated in vacuo to about 10 mL and diluted with *n*-hexane (50 mL). After cooling for 12 h at −10 °C a bright orange crystalline solid was isolated and dried in vacuo. Yield 4.20 g (87 %). Crystals of the *fac* isomer suitable for X-ray analysis were obtained upon recrystallization from a mixture of light petroleum and dichloromethane (4:1) at −10 °C (vide infra). IR (CH_2Cl_2): 1978, 1886 [ν(CO)] cm^{-1}. IR (nujol): 2437, 2405, 2284 [ν(BH_2)]; 1971, 1877 [ν(CO)] cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.24 [s, 3 H, $NC_5H_4CH_3$], 2.34 [s, 6 H, $C_6H_3(CH_3)_2$], 6.14−6.18 [m, 2 H, H-4($C_3H_3N_2$)], 6.85 [d, 2 H, H-3,5(C_6H_3)], 7.05 [t, 1 H, H-4(C_6H_3)], 7.20−8.00 [m, 10 H, H-3,5($C_3H_3N_2$) and H-2,3,5,6(NC_5H_4)] ppm. ^{13}C{^{1}H} NMR: δ = 294.5 (major W≡C), 284.5 (minor W≡C), 225.3 (major WCO), 227.5 (minor WCO), 221.5 (minor WCO), 150.8 [C-4(NC_5H_4)], 145.4 [C-3($C_3H_3N_2$)], 140.5 [C-4(C_6H_3)], 136.6 [C-5($C_3H_3N_2$)], 127.3 [C-2,6(C_6H_3)], 127.0 [C-3,5(C_6H_3)], 125.9 [C-3,5(NC_5H_4)], 105.4 [C-4($C_3H_3N_2$)], 21.2 [$NC_5H_4CH_3$], 20.6 [$C_6H_3CH_3$] ppm. FAB-MS: *m*/*z* (%) = 597(33) [M]$^+$, 569(80) [M − CO]$^+$, 541(35) [M − 2CO]$^+$, 503(41) [M − pic]$^+$, 446(19) [M − 2CO-pic]$^+$. $C_{23}H_{24}BN_5O_2W$: calcd. C 46.26, H 4.05, N 11.73; found C 45.6, H 3.9, N 10.9.

Synthesis of *fac*- and *mer*-$[W(\equiv CC_6H_2Me_3\text{-}2,4,6)(CO)_2(NC_5H_4\text{-}Me\text{-}4)\{H_2B(pz)_2\}]$ (2b): The compound *trans,cis,cis*-$[W\equiv CC_6H_2Me_3\text{-}2,4,6)Br(CO)_2(NC_5H_4Me\text{-}4)_2]$ (**1b**, 5.00 g, 7.80 mmol) was treated as above to afford an orange powder. Yield 4.20 g (88 %). IR (CH_2Cl_2): 1975, 1888 [ν(CO)] cm^{-1}. IR (nujol): 2425, 2351, 2287 [ν(BH_2)]; 1971, 1874 [ν(CO)] cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 2.16 (s, 3 H, $C_6H_2CH_3$-4), 2.29 (s, 3 H, $NC_5H_4CH_3$), 2.32 (s, 6 H, $C_6H_2CH_3$-2,6), 6.14−6.17 [m, 2 H, H-4($C_3H_3N_2$)], 6.67 [s, 2 H, H-3,5(C_6H_2)], 7.20−8.00 [m, 8 H, H-3,5($C_3H_3N_2$) and H-2,3,5,6(NC_5H_4)] ppm. ^{13}C{^{1}H} NMR: δ = 295.0 [major W≡C, ^1J(WC) = 200 Hz], 284.9 [minor W≡C, ^1J(WC) = 194 Hz], 225.5 [major WCO, ^1J(WC) = 169 Hz], 227.6 [minor WCO, ^1J(WC) = 169 Hz], 221.9 [minor WCO, ^1J(WC) = 169 Hz], 150.8 [C-4(NC_5H_4)], 145.4 [C-3($C_3H_3N_2$)], 136.5 [C-5($C_3H_3N_2$)], 127.8 [C-3,5(C_6H_3)], 125.9 [C-3,5(NC_5H_4), 125.6 [C-2,6(C_6H_2)], 105.4 [C-4($C_3H_3N_2$)], 21.2, 20.8 [$NC_5H_4CH_3$ and $C_6H_2CH_3$-4)], 20.6 [$C_6H_2CH_3$-2,6] ppm. FAB-MS: *m*/*z* (%) = 610 (33) [M]$^+$, 583 (41) [M − CO]$^+$, 555 (24) [M − 2CO]$^+$, 516 (100) [M − pic]$^+$, 488 (20) [M − CO − pic]$^+$, 460 (57) [M − pic − 2CO]$^+$. $C_{24}H_{26}BN_5O_2W$: calcd. C 47.17, H 4.29, N 11.46; found C 47.6, H 4.0, N 11.8.

Synthesis of $[W(\equiv CC_6H_3Me_2\text{-}2,6)(CO)_2(CNC_6H_3Me_2\text{-}2,6)\text{-}\{H_2B(pz)_2\}]$ (3a): The compound *trans,cis,cis*-$[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(CNC_6H_3Me_2\text{-}2,6)_2]$ (**5a**, 0.20 g, 0.30 mmol) was dissolved in a mixture of diethyl ether and petroleum ether (9:1,

30 mL) to which 1.1 equivalents of $K[H_2B(pz)_2]$ (0.06 g, 0.33 mmol) was subsequently added. The mixture was stirred for 4 h in the absence of light. The resulting red solution was concentrated under reduced pressure and purified on a silica-gel loaded column (2 × 30 cm, −40 °C) eluting with a mixture of dichloromethane and light petroleum (1:1). The red fraction was collected and the solvent removed in vacuo under the exclusion of light, to provide a glassy thermally sensitive red solid. Yield 0.16 g (84 %). IR (CH_2Cl_2): 2141 [ν(CN)]; 1998, 1923 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 2.14 [s, 6 H, $NC_6H_3(CH_3)_2$], 2.66, 2.68 (s × 2, 6 H, $CC_6H_3CH_3$), 6.17 [m, 2 H, H-4($C_3H_3N_2$)], 6.96 [d, 2 H, H-3,5(CC_6H_3)], 7.00 [m, 3 H, H-3,5(NC_6H_3)], 7.09 [t, 1 H, H-4(C_6H_3)], 7.58−7.80 [m, 4 H, H-3,5($C_3H_3N_2$)] ppm. $^{13}C\{^1H\}$ NMR: δ = 287.5 (W≡C), 221.7, 210.6 (WCO), 168.0 (WCN), 146.8 [C-1(CC_6H_3)], 145.4 [C-1(NC_6H_3)], 145.0, 143.8 [C-5($C_3H_3N_2$)], 136.1, 135.2 [C-3($C_3H_3N_2$)], 127.9 [C-3,5(CC_6H_3)], 127.2 [C-3,5(NC_6H_3)], 105.2, 104.9 [C-4($C_3H_3N_2$)], 18.7, 18.2 [$NC_6H_3(CH_3)_2$ and $C_6H_3(CH_3)_2$] ppm. Satisfactory elemental and FAB-MS data not obtained due to thermal and photolytic lability.

Synthesis of [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(CNCMe$_3$){H$_2$B(pz)$_2$}] (3b): The salt $K[H_2B(pz)_2]$ (0.06 g, 0.33 mmol, 1.1 equiv.) was added to *trans,cis,cis*-[W(≡$CC_6H_3Me_2$-2,6)Br$(CO)_2(CNCMe_3)_2$] (**5c**, 0.20 g, 0.30 mmol) in a mixture of diethyl ether and petroleum ether (9:1, 30 mL). The suspension was stirred for 4 h. under the exclusion of light. The resulting claret solution was concentrated under reduced pressure and purified on a silica gel loaded column (2 × 30 cm, −40 °C) eluting with a mixture of CH_2Cl_2 and light petroleum (1:1). The red fraction was collected and the solvent removed in vacuo (still in the absence of light). An amorphous red solid was obtained. Yield 0.12 g (67 %). IR (CH_2Cl_2): 2175 [ν(CN)]; 1998, 1918 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.16 (s, 9 H, CMe_3), 2.50 (s, 6 H, $C_6H_3CH_3$), 5.99 [dd, 1 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2 Hz], 6.02 [dd, 1 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2 Hz], 6.80 (m × 2, 3 H, C_6H_3), 7.40−8.80 [m, 4 H, H-3,5($C_3H_3N_2$)] ppm. $^{13}C\{^1H\}$ NMR: δ = 285.6 (W≡C), 222.1, 211.2 (WCO), 144.3, 143.2 [C-5($C_3H_3N_2$)], 136.1, 135.5 [C-3($C_3H_3N_2$)], 126.9 [C-2,6(C_6H_3)], 126.6 [C-3,5(C_6H_3)], 147.8 [C-1(C_6H_3)], 139.6 [C-4(C_6H_3)], 104.8, 104.5 [C-4($C_3H_3N_2$)], 56.2 [$C(CH_3)_3$], 29.9 [$C(CH_3)_3$], 20.4 [$C_6H_3(CH_3)_2$] ppm. Satisfactory elemental analytical data not obtained due to thermal and photochemical lability.

Synthesis of [W(η^2-OCCC$_6$H$_3$Me$_2$-2,6)(CO)(CNCMe$_3$)$_2${H$_2$B(pz)$_2$}] (4b): *tert*-Butyl isocyanide (0.40, mL, 0.735 gcm^{-3}, 0.54 g, 6.50 mmol) was added to [W(≡$CC_6H_3Me_2$-2,6)$(CO)_2(NC_5H_4$Me-4){$H_2B(pz)_2$}] (**2a**, 0.50 g, 0.84 mmol) in dichloromethane (30 mL). The mixture was then irradiated for 3 h with stirring at 0 °C (ice bath). The resulting purple solution was concentrated to about 10 mL and purified on a silica-gel loaded column (2 × 30 cm, −40 °C) eluting initially with a mixture of CH_2Cl_2 and light petroleum (1:1) to remove orange [W(≡$CC_6H_3Me_2$-2,6)-$(CO)_2(CNCMe_3)${$H_2B(pz)_2$}] (**3b**, vide supra). The purple fraction containing **4b** was then eluted with tetrahydrofuran. The resulting eluate was concentrated under reduced pressure to about 2 mL, diluted with light petroleum (10 mL) and stored at −10 °C whereupon purple thermally sensitive microcrystals were obtained overnight. Yield 0.23 g (41 %). IR (CH_2Cl_2): 2162 [ν(CN)]; 1912 [ν(C≡O)]; 1699 [ν(C=O)] cm^{-1}. IR (nujol): 2405 [ν(BH)]; 2160 [ν(CN)]; 1917 [ν(C≡O)]; 1708 [ν(C=O)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.27 (s, 18 H, CMe_3), 2.02 [s, 6 H, $C_6H_3(CH_3)_2$], 6.02, 6.27 [dd × 2, 2 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2, 2 Hz], 7.00 [m, 3 H, C_6H_3], 7.58, 7.59, 7.64, 8.08 [d × 4, 4 H, H-3,5($C_3H_3N_2$)] ppm. $^{13}C\{^1H\}$ NMR: 247.3 (WCO), 217.2 (W=*C*CO), 208.8 (W=C*C*O), 153.0 (WCN), 144.9 [C-1(C_6H_3)], 147.0, 144.3 [C-3($C_3H_3N_2$)], 137.1, 135.9 [C-5($C_3H_3N_2$)], 127.1 [C-3,5(C_6H_3)], 126.2 [C-2,6(C_6H_3)], 104.8, 106.1 [C-4($C_3H_3N_2$)], 58.0 (CMe_3), 29.9 [$C(CH_3)_3$], 21.1 [$C_6H_3(CH_3)_2$] ppm. FAB-MS: *m*/*z* (%) = 671 (21) $[M]^+$, 641 (20) $[M - CO]^+$, 614 (100) $[M - 2CO]^+$, 588 (14) $[M - CNR']^+$, 559 (56) $[M - CO - CNR']^+$, 531 (16) $[M - 2CO - CNR']^+$. Satisfactory elemental data were not obtained due to the thermal instability. $C_{27}H_{35}BN_6O_2W$: calcd. C 48.38, H 5.26, N 12.54; found 45.5, H 4.4, N 11.3.

Synthesis of [W(≡CC$_6$H$_3$Me$_2$-2,6)Br(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_2$] (5a): 2,6-Dimethylphenyl isocyanide (0.45 g, 3.4 mmol) was added to *trans,cis,cis*-[W(≡$CC_6H_3Me_2$-2,6)Br$(CO)_2(NC_5H_4$Me-4)$_2$] (**1a**, 1.00 g, 1.70 mmol) in diethyl ether (30 mL) and the mixture stirred for 15 h after which time the solvent was removed in vacuo. The resulting pale yellow solid was redissolved in *n*-hexane (10 mL) and filtered through diatomaceous earth. The filtrate was further diluted with hexane (15 mL) and cooled to −10 °C for 2 days during which time fine yellow needles formed which were isolated by decantation and dried in vacuo. Yield 0.98 g (89 %). IR (CH_2Cl_2): 2159, 2134 [ν(CN)]; 2021, 1974 [ν(CO)] cm^{-1}. IR (nujol): 2162, 2135 [ν(CN)]; 2005, 1959 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 2.48 [s, 12 H, $NC_6H_3(CH_3)_2$], 2.58 [s, 6 H, $CC_6H_3(CH_3)_2$], 6.90, 6.92 [d × 2 H, H-3,5(C_6H_3)], 7.1 [m, 1 H, H-4(C_6H_3)] ppm. $^{13}C\{^1H\}$ NMR: δ = 269.7 [W≡C, ^1J(WC) = 189 Hz], 205.0 [WCO, ^1J(WC) = 136 Hz], 167.7 (br., C≡N), 161.8 (br., N-C), 150−124 (NC_6H_3 and CC_6H_3), 21.2 [$CC_6H_3(CH_3)_2$], 18.8 [$NC_6H_3(CH_3)_2$] ppm. FAB- MS: *m*/*z* (%) = 700 (12) $[M]^+$, 672 (58) $[M - CO]^+$, 644 (46) $[M - 2CO]^+$. Calcd for $C_{29}H_{27}BrO_2N_2W$: calcd. C 49.81, H 3.89, N 4.01; found C 50.0, H 4.1, N 3.9.

Synthesis of [W(≡CC$_6$H$_2$Me$_3$-2,4,6)Br(CO)$_2$(CNC$_6$H$_3$Me$_2$-2,6)$_2$] (5b): 2,6-Dimethylphenyl isocyanide (0.45 g, 3.40 mmol) was added to *trans,cis,cis*-[W(≡$CC_6H_2Me_3$-2,4,6)Br$(CO)_2(NC_5H_4$Me-4)$_2$] (**1b**, 1.00 g, 1.70 mmol) in diethyl ether (30 mL). The mixture was stirred for 15 h, after which time the solvent and γ-picoline were removed in vacuo. The resulting pale yellow solid was redissolved in hexane (10 mL) and filtered through diatomaceous earth. Light petroleum ether (15 mL) was added to the yellow filtrate and the mixture stored at −10 °C for 2 days, whereupon fine yellow crystalline needles were obtained and dried in vacuo. Yield 1.00 g (88 %). IR (CH_2Cl_2): 2158, 2132 [ν(CN)]; 2018, 1972 [ν(CO)] cm^{-1}. IR (nujol): 2162, 2134 [ν(CN)]; 2006, 1955 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 2.18 (s, 3 H, $CC_6H_2CH_3$-4), 2.50 [s, 12 H, $NC_6H_3(CH_3)_2$], 2.56 [s, 6 H $CC_6H_2(CH_3)_2$-2,6] ppm. $^{13}C\{^1H\}$ NMR: δ = 270.5 [W≡C, ^1J(WC) = 189 Hz], 204.9 [WCO, ^1J(WC) = 136 Hz], 162.2 (br., WCN), 147.2 [C-1(C_6H_2)], 140.6 [C-2,6(C_6H_3)], 138.5[C-2,6(C_6H_2)], 135.6 [C-3,5(C_6H_2)], 129.3 [C-4(C_6H_3)], 128.0 [C-3,5(C_6H_3)], 126.6 [C-4(C_6H_2)], 21.6 [$C_6H_2CH_3$-4], 21.1, 19.0 [$NC_6H_3(CH_3)_2$-2,6 and $CC_6H_2(CH_3)_2$-2,6] ppm. FAB-MS: *m*/*z* (%) = 658 (100) $[M - 2CO]^+$. $C_{30}H_{29}BrN_2O_2W$: calcd. C 50.51, H 4.10, N 3.93; found C 50.2, H 4.0, N 3.9.

Synthesis of [W(≡CC$_6$H$_3$Me$_2$-2,6)Br(CO)$_2$(CNCMe$_3$)$_2$] (5c): *tert*-Butyl isocyanide (0.40 mL, 0.795 $gmol^{-1}$, 0.50 g, 6.0 mmol, excess) was added to *trans,cis,cis*-[W(≡$CC_6H_3Me_2$-2,6)Br$(CO)_2(NC_5H_4$Me-4)$_2$] (**1a**, 1.00 g, 1.70 mmol) in diethyl ether (30 mL) and the mixture stirred for 15 h. The resulting pale yellow solution was reduced to dryness in vacuo and light petroleum (50 mL) was added to the residue. The resulting solution was cooled to −10 °C for 12 h whereupon a bright yellow crystalline solid was isolated and dried in vacuo. Further crops were obtained by concentrating the supernatant liquor, though these were generally less pure. Yield 0.70 g (73 %). IR (CH_2Cl_2): 2158, 2132 [ν(CN)]; 2018, 1972 [ν(CO)] cm^{-1}. IR (nujol): 2162, 2134 [ν(CN)]; 2006, 1955 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.57 [s, 18 H,

CMe_3], 2.52 [s, 6 H, $C_6H_3(CH_3)_2$], 6.90 [d, 2 H, H-3,5(C_6H_3)], 7.10 [t, 1 H, H-4(C_6H_3)] ppm. $^{13}C\{^1H\}$ NMR: δ = 267.1 [W≡C, ^1J (WC) = 189 Hz], 206.8 [WCO, ^1J (WC) = 135 Hz], 147.0 (br., WC≡N), 146.1 [C-1(C_6H_3)], 140.3 [C-4(C_6H_3)], 127.4 [C-2,6(C_6H_3)], 127.2 [C-3,5(C_6H_3)], 57.4 [CMe_3], 30.5 [$C(CH_3)_3$], 20.8 [$C_6H_3(CH_3)_2$] ppm. FAB-MS: *m/z* = 606 $[M]^+$, 576 $[M - CO]^+$, 548 $[M - 2CO]^+$, 523 $[M - CNR]^+$, 492 $[M - CO - CNR]^+$. $C_{21}H_{27}BrN_2O_2W$: calcd. C 41.81, H 4.51, N 4.64; found C 41.7, H 4.4, N 4.5.

Synthesis of *fac*-[W(≡$CC_6H_3Me_2$-2,6)(CO)$_2$(PMe_2Ph){$H_2B(pz)_2$}] (6a): Dimethylphenylphosphane (0.12 mL, 0.97 gmL^{-1}, 0.12 g, 0.87 mmol) was added to *mer/fac*-[W(≡$CC_6H_3Me_2$-2,6)-(CO)$_2$(NC_5H_4Me-4){$H_2B(pz)_2$}] (**2a**, 0.50 g, 0.84 mmol) in dichloromethane (30 mL) and the mixture stirred for 12 h. The resulting orange solution was concentrated to about 10 mL and chromatographed on a silica-gel loaded column (2 × 30 cm, −30 °C) eluting with a mixture of dichloromethane and light petroleum ether (1:1). The major orange fraction was collected and concentrated under reduced pressure to about 10 mL and then diluted with diethyl ether (50 mL). This solution was cooled to −10 °C whereupon an orange microcrystalline solid was obtained. Yield 0.52 g (95 %). Crystals suitable for X-ray analysis were obtained upon recrystallization from hexane/propanone (4:1) at −10 °C. NB: The reaction is sufficiently clean that for most practical purposes the chromatography step may be omitted in which case, the solvent is simply removed and the resulting orange powder washed with light petroleum (10 mL) and dried thoroughly under high vacuum to remove liberated γ-picoline and unchanged phosphane. IR (CH_2Cl_2): 1992, 1903 [ν(CO)] cm^{-1}. IR (nujol): 2407, 2345, 2288 [ν(BH_2)]; 1974, 1885 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.21, 1.31 [d × 2, 6 H, $^2J_{P,H}$ = 7.3 Hz, diastereotopic-PMe_2], 2.63 (s, 6 H, $C_6H_3CH_3$), 3.55 (br, BH_2), 6.12, 6.16 [dd × 2, 2 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2, 2 Hz], 6.96−7.10 [m, 3 H, H-4(C_6H_3)], 7.24−7.28 (m, 5 H, C_6H_5), 7.36, 7.56, 7.66, 7.89 [d × 4, 4 H, H-3,5($C_3H_3N_2$), $^3J_{H,H}$ = 2 Hz] ppm. $^{13}C\{^1H\}$ NMR: δ = 285.1 (d, W≡C, $^2J_{P,C}$ = 8.9 Hz), 227.0 (d, WCO, $^2J_{P,C}$ = 3.6 Hz), 213.4 (d, WCO, $^2J_{P,C}$ = 53.5 Hz), 144.9, 143.6 [C-3($C_3H_3N_2$)], 137.0, 136.8 [C-5($C_3H_3N_2$)], 135.7 [C-1(C_6H_5)], 130.8, 130.6 [C-2,6(C_6H_5)], 129.6−127.3 [C_6H_5 and C_6H_3], 105.4, 105.1 [C-4($C_3H_3N_2$)], 20.9 [$C_6H_3(CH_3)_2$], 15.7, 14.5 [d × 2, $^1J_{P,C}$ = 24 Hz, diastereotopic-$P(CH_3)_2$] ppm. $^{31}P\{^1H\}$ NMR: δ = −4.1 ppm [^1J(WP) = 230.6 Hz] ppm. FAB-MS: *m/z* (%) = 641 (14) $[M - H]^+$, 614 (90) $[M - CO]^+$, 584 (21) $[M - 2CO]^+$, 503 (11) $[M - PMe_2Ph]^+$. $C_{25}H_{28}BN_4O_2PW$: calcd. C 46.76, H 4.40, N 8.72; found C 46.2, H 4.2, N, 8.5.

Synthesis of *fac*-[W(≡$CC_6H_3Me_3$-2,4,6)(CO)$_2$(PMe_2Ph)-{$H_2B(pz)_2$}] (6b): This complex was prepared as described for **6a** (see above) from *mer/fac*-[W≡$CC_6H_2Me_3$-2,4,6)(CO)$_2$(NC_5H_4Me-4){$H_2B(pz)_2$}] (**2b**, 0.51 g, 0.84 mmol). Yield 0.53 g (95 %). IR (CH_2Cl_2): 1993, 1905 [ν(CO)]. IR (nujol): 2407, 2345, 2288 [ν(BH_2)]; 1976, 1882 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.19, 1.34 [d × 2, 6 H, diastereotopic-PMe_2, $^2J_{P,H}$ = 7.1 Hz], 2.23 [s, 3 H, $C_6H_2CH_3$-4], 2.60 [s, 6 H, $C_6H_2(CH_3)_2$-2,6], 6.12, 6.16 [dd × 2, 2 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2, 2 Hz], 6.78 [s, 2 H, H-3,5(C_6H_2)], 7.28 (m, 5 H, C_6H_5), 7.34, 7.56, 7.66, 7.79 [d × 4, 4 H, H-3,5($C_3H_3N_2$), $^3J_{H,H}$ = 2 Hz] ppm. $^{13}C\{^1H\}$ NMR: δ = 284.4 [d, W≡C, $^2J_{P,C}$ = 8.6 Hz], 227.1 [WCO, $^2J_{P,C}$ = 3.6 Hz], 213.4 [d, WCO, $^2J_{P,C}$ = 53.1 Hz], 144.9, 143.6 [C-3($C_3H_3N_2$)], 137.0, 136.8 [C-5($C_3H_3N_2$)], 135.7 [C-1(C_6H_5), $^1J_{P,C}$ = 36 Hz], 130.7, 130.6 [C-2,6(C_6H_5)], 128.4, 128.2 [C-3,5(C_6H_5)], 127.7 [C-2,6(C_6H_2)], 127.3 [C-3,5(C_6H_3)], 105.4, 105.1 [C-4($C_3H_3N_2$)], 21.5 ($C_6H_2CH_3$-4), 20.9 [$C_6H_3(CH_3)_2$-2,6], 15.5, 14.5 [diastereotopic-$P(CH_3)_2$, $^1J_{P,C}$ = 24 Hz] ppm. $^{31}P\{^1H\}$ NMR: δ = −4.2 ppm [$^1J_{W,P}$ = 230.6 Hz]. FAB-MS: *m/z* (%) = 641 (8) $[M]^+$, 614 (75) $[M - CO]^+$, 584 (11) $[M - 2CO]^+$. Elemental microanalytical data not acquired.

Synthesis of *cis,trans,cis*-[W(≡$CC_6H_2Me_3$-2,4,6)(CO)(PMe_2Ph)$_2$-{$H_2B(pz)_2$}] (7): (a) Dimethylphenylphosphane (0.24 g, 1.60 mmol) was added to *mer/fac*-[W(≡$CC_6H_2Me_3$-2,4,6)(CO)$_2$(NC_5H_4Me-4){$H_2B(pz)_2$}] (**2b**, 0.50 g, 0.82 mmol) in dichloromethane (30 mL). The mixture was stirred for 12 h and the resulting red solution was then concentrated to about 10 mL under reduced pressure and purified on silica-gel (2 × 30 cm, −30 °C) eluting with a dichloromethane/light petroleum (1:1) mixture. The red eluate was concentrated in vacuo to about 10 mL and diluted with diethyl ether (50 mL). This solution was cooled to −10 °C whereupon a red crystalline solid was obtained, isolated by decantation and dried in vacuo. Yield 0.60 g (95 %). (b) A mixture of *mer*-[W(≡$CC_6H_2Me_3$-2,4,6)Br(CO)(PMe_2Ph)$_3$] (**8**, 0.50 g, 0.60 mmol) and K[$H_2B(pz)_2$] (0.12 g, 0.65 mmol) in dichloromethane (30 mL) was stirred for 1 h. The mixture was then purified as described in (a) (see above) to provide **7**. Yield 0.46 g (93 %). IR (CH_2Cl_2): 1860 [ν(CO)] cm^{-1}. IR (nujol): 2424, 2390, 2353, 2284 [ν(BH_2)]; 1857 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.40, 1.47 [vt × 2, 12 H, *trans*-$(PMe_2)_2$, $^{2,4}J_{P,H}$ ca. 3 Hz], 2.19 [s, 3 H, $C_6H_2CH_3$-4], 2.49 [s, 6 H, $C_6H_2(CH_3)_2$-2,6], 5.98, 6.11 [dd × 2, 2 H, H-4($C_3H_3N_2$), $^3J_{H,H}$ = 2, 2 Hz], 6.69 (s, 2 H, C_6H_2), 7.08−7.26 (m, 10 H, C_6H_5), 7.36, 7.44, 7.58, 7.85 [d × 4, 4 H, H-3,5($C_3H_3N_2$), $^3J_{H,H}$ = 2 Hz] ppm. $^{13}C\{^1H\}$ NMR: δ = 278.2 (t, W≡C, $^2J_{P,C}$ = 11 Hz), 249.9 (t, WCO, $^2J_{P,C}$ = 5.3 Hz), 144.9, 143.6 [C-3($C_3H_3N_2$)], 136.5, 136.1 [C-5($C_3H_3N_2$)], 135.7 [C-1(C_6H_5), $^1J_{P,C}$ = 36.0 Hz], 130.6 [C-3,5(C_6H_2)], 130.5−127.5 [C-3,5(C_6H_5)], 104.9, 104.6 [C-4($C_3H_3N_2$)], 21.6 [$C_6H_2CH_3$-4)], 20.6 [$C_6H_2(CH_3)_2$-2,6], 17.9 [vt, $P(CH_3)_2$, $^{1,3}J_{P,C}$ = 13.4 Hz] ppm. $^{31}P\{^1H\}$ NMR: δ = 0.28 [$^1J_{W,P}$ = 281.4 Hz] ppm. FAB-MS: *m/z* (%) [assignment] = 766 (12) $[M]^+$, 738 (4) $[M - CO]^+$, 628 (100) $[M - PMe_2Ph]^+$, 598 (35) $[M - PMe_2Ph - CO]^+$, 459 (10) $[M - 2PMe_2Ph - CO]^+$. $C_{33}H_{41}BN_4OP_2W$: calcd. C 51.72, H 5.39, N 7.31; found C 52.1, H 5.7, N 6.8.

Synthesis of *mer*-[W(≡$CC_6H_2Me_3$-2,4,6)Br(CO)(PMe_2Ph)$_3$] (8): NB − the related complex *mer*-[W(≡CPh)Cl(CO)(PMe_3)$_3$] has been described previously by Mayr.[27] Dimethylphenylphosphane (0.70 g, 5.10 mmol) was added to *trans,cis,cis*-[W(≡$CC_6H_2Me_3$-2,4,6)Br(CO)$_2$(NC_5H_4Me-4)$_2$] (**1b**, 1.00 g, 1.70 mmol) in diethyl ether (30 mL) and the mixture stirred for 15 h. The resulting pale yellow solution was filtered though diatomaceous earth (20 × 30 mm). The yellow filtrate was then diluted with light petroleum (15 mL) and cooled to −10 °C for 2 days, whereupon a fine yellow powder was obtained which was isolated by decantation and dried in vacuo. Subsequent recrystallisation from a mixture of dichloromethane/petroleum ether (−20 °C) afforded bright yellow needles. Yield 1.01 g (90 %). IR (CH_2Cl_2): 1905 [ν(CO)] cm^{-1}. IR (nujol): 1900 [ν(CO)] cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.34−2.14 [m, 21 H, PMe_2 and $C_6H_2CH_3$-4], 2.19 [s, 6 H, $C_6H_2(CH_3)_2$-2,6], 6.68 [s, 2 H, H-3,5(C_6H_2)], 6.85−7.55 [m, 15 H, C_6H_5] ppm. $^{13}C\{^1H\}$ NMR: δ = 267.7 (dt, W≡C, $^2J_{P,C}$ = 7, 12 Hz), 233.3 [dt, WCO, *trans*- $^2J_{P,C}$ = 27, *cis*- $^2J(P_2C)$ = 7 Hz], 134.5−127.9 (C_6H_5 and, C_6H_2), 22.75 [vt, *trans*-diastereotopic-$W(PMe_2)_2$, $^{1,3}J(P_2C)$ = 15.1 Hz], 21.91 [$C_6H_2(CH_3)_2$-2,6], 21.41 ($C_6H_2CH_3$-4), 17.63 [vt, *trans*-diastereotopic-$W(PMe_2)_2$, $^{1,3}J(P_2C)$ = 13.4 Hz], 16.89 [d, unique-PMe_2, $^1J_{P,C}$ = 25.0 Hz] ppm. $^{31}P\{^1H\}$ NMR: δ = −15.0 [d, ^1J(WP) = 268, $^2J_{P,P}$ = 20], −22.5 [t, ^1J(WP) = 230, $^2J_{P,P}$ = 20 Hz] ppm. FAB-MS: *m/z* (%) = 700 (44) $[M - PMe_2Ph]^+$, 672 (100) $[M - CO - PMe_2Ph]^+$, 532 (14) $[M - CO - 2PMe_2Ph]^+$. $C_{35}H_{44}BrOP_3W \cdot 0.5CH_2Cl_2$: calcd. C 48.46, H 5.16; found C 48.6, H 5.0.

Crystal Data, X-ray Data Collection and Structural Determination (a) [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(NC$_5$H$_4$Me-4){H$_2$B(pz)$_2$}]·0.5CH$_2$Cl$_2$ (2a·0.5CH$_2$Cl$_2$): Orange/red blocks were grown by prolonged cooling of a saturated solution of the complex in a mixture of dichloromethane and petroleum ether (bp. 40−60 °C). Crystal data for **2a**: $C_{23}H_{24}BN_5O_2W·0.5CH_2Cl_2$, M_r = 639.6 g·mol^{-1}, monoclinic, $P2_1/c$ (no. 14), a = 9.463(3), b = 19.153(2), c = 16.228(3) Å, β = 105.41(2)°, V = 2835.6(10) Å^3, Z = 4, D_c = 1.498 g cm^{-3}, μ(Mo-K_α) = 4.19 mm^{-1}, T = 293 K, 3673 independent measured reflections, F^2 refinement, R_1 = 0.032, wR_2 = 0.087, 3081 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, 2θ ≤ 45°], 329 parameters.
(b) [W(≡CC$_6$H$_3$Me$_2$-2,6)(CO)$_2$(PMe$_2$Ph){H$_2$B(pz)$_2$}] (6a): Yellow needles were grown by cooling (−10 °C) a saturated solution of the complex in a mixture of propanone and light petroleum. Crystal data for **6a**: $C_{25}H_{28}BN_4O_2PW$, M_r = 642.1 g·mol^{-1}, monoclinic, $P2_1/n$ (no. 14), a = 9.982(1), b = 16.952(2), c = 15.970(2) Å, β = 103.31(1)°, V = 2629.6(5) Å^3, Z = 4, D_c = 1.622 g cm^{-3}, μ(Cu-K_α) = 8.94 mm^{-1}, T = 293 K, 3664 independent measured reflections, F^2 refinement, R_1 = 0.022, wR_2 = 0.054, 3385 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, 2θ ≤ 116°], 298 parameters. CCDC-219536 (**2a**) and −219537 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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