The Chemistry of New Nitrosyltungsten Complexes with Pyridyl-Functionalized Phosphane Ligands

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The coordination chemistry of pyridylphosphanes, such as 2-(6-*tert*-butylpyridyl)diphenylphosphane (Ph_2P-*tert*-Bupy) (**6**) and 2-(6-*tert*-butylpyridyl)dimethylphosphane (Me_2P-*tert*-Bupy) (**7**) towards a number of nitrosyltungsten complexes is reported. Displacement of the loosely coordinated MeCN from $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ led to the following cationic compounds incorporating mono- and bidentate coordinated phosphane ligands: *cis*,*cis*-$[W(CO)_2(NO)(Ph_2PR)(\eta^2\text{-}Ph_2PR)][BF_4]$, [R = 2-pyridyl (**9a**), 2-picolyl (**11**)], *cis*,*cis*-$[W(CO)(NO)(\eta^2\text{-}Ph_2Ppy)_2][BF_4]$ (**20**), *trans*,*trans*-$[W(CO)(NO)(\eta^2\text{-}Ph_2Ppy)_2][BPh_4]$ (**21**), *fac*-$[W(CO)_2(NO)(Me_2Ppy)_3][BF_4]$ (**16**), *fac*-$[W(CO)_2(NO)(Me_2P\text{-}tert\text{-}Bupy)_3][BF_4]$ (**18**), *cis*,*cis*-$[W(CO)_2(NO)(Me_2Ppy)(\eta^2\text{-}Me_2Ppy)][BF_4]$ (**22**), and *cis*,*cis*-$[W(CO)_2(CH_3CN)(NO)(Me_2P\text{-}tert\text{-}Bupy)_2][BF_4]$ (**23a**). The cationic complex *cis*,*mer*-$[W(CO)_3(NO)(Ph_2P\text{-}tert\text{-}Bupy)_2][PF_6]$ (**14**) has been prepared by nitrosylation of *cis*/*trans*-$W(CO)_4(Ph_2P\text{-}tert\text{-}Bupy)_2$ (**13**). Reactions of **9a**, **11**, **14**, **16**, and **18** with hydride transfer reagents afforded *trans*,*trans*-$HW(CO)_2(NO)(Ph_2Ppy)_2$ (**10**), *trans*,*trans*-$HW(CO)_2(NO)(Ph_2Ppic)_2$ (**12**), *trans*,*trans*-$HW(CO)_2(NO)(Ph_2\text{-}tBupy)_2$ (**15**), *cis*/*trans*-$HW(CO)_2(NO)(Me_2Ppy)_2$ (**17**), and *cis*/*trans*-$HW(CO)_2(NO)(Me_2P\text{-}tert\text{-}Bupy)_2$ (**19**), respectively. Reactivity experiments with acetic acid, hydroiodic acid, carbon dioxide, and acetylenedicarboxylic acid were performed, and were found to afford *trans*-$W(CO)(NO)(Ph_2Ppy)_2(\eta^2\text{-}CH_3CO_2)$ (**24**), *trans*,*trans*-$IW(CO)_2(NO)(Ph_2Ppy)_2$ (**25**), *trans*-$W(HCO_2)(CO)_2(NO)(Ph_2Ppy)_2$ (**26**), and *trans*-$W\{\eta^2\text{-}(Z)\text{-}C(CO_2Me){=}CH[C(O)OMe]\}(CO)(NO)(Ph_2Ppic)_2$ (**27**), respectively. The influence of the pyridyl substituent in **10** was probed by a comparative H/D exchange experiment in which **10** and the analogous complex $HW(CO)_2(NO)(PPh_3)_2$ were treated with MeOD. The deuterated complex *trans*,*trans*-$WD(CO)_2(NO)(Ph_2Ppy)_2$ (**28**) could be isolated. The structures of **9a**, **11**, **14**, and **20** have been determined by single-crystal X-ray diffraction analysis.

Introduction

Previously, we have demonstrated that nitrosyltungsten hydride complexes are efficient reducing agents for aldehydes and ketones, the best results being achieved in the presence of a weak acid.[1−3] Furthermore, it has been shown that O−H and N−H bonds can act as weak acid components towards weakly basic M−H bonds.[4−8] Thus, intramolecular H···H interactions may be established, which could also play an important role in the heterolytic splitting of dihydrogen.[9] The pyridylphosphane ligand offers the possibility of either abstracting a proton from an external source or of activating a dihydrogen ligand coordinated to an unsaturated metal centre.[10] Therefore, this base-promoted splitting of dihydrogen through formation of a (ligand−H^+)−(metal−H^-) intermediate is of great significance with regard to catalytic ionic hydrogenations, as recently described by Noyori.[11,12] In order to design such a bifunctional system, we set out to prepare a series of cationic nitrosyltungsten and nitrosyltungsten hydride species having basic pyridyl substituents present in their coordination spheres. Similar investigations with P,N-, P,O-, and P,S-hybrid ligands have been described previously.[13−15]

Results and Discussion

Preparation of Pyridyl-Substituted Phosphane Ligands

Diphenylpyridylphosphane (Ph_2Ppy)[16] and dimethylpyridylphosphane (Me_2Ppy)[17] were prepared according to literature procedures. On the other hand, new methods were developed for the synthesis of phosphanes bearing bulkier pyridyl substituents. Thus, the picolyl-substituted derivative 2-(6-methylpyridyl)diphenylphosphane (Ph_2Ppic) was synthesized by a route different from that reported in the literature[18] by adding 6-chloro-2-picoline to a solution of $LiPPh_2$, prepared from *n*-butyllithium and diphenylphosphane. For the preparation of the *tert*-butyl-substituted phosphanes, 2-(6-*tert*-butylpyridyl)diphenylphosphane (Ph_2P-*tert*-Bupy) and 2-(6-*tert*-butylpyridyl)dimethylphosphane (Me_2P-*tert*-Bupy), the starting material 2-*tert*-butyl-6-chloropyridine was synthesized according to a method described by Mariella for analogous compounds.[19]

Preparation of the Cationic Complexes

With the exception of the bulkiest phosphane, Ph_2P-*tert*-Bupy, the best yields of the cationic metal complexes were

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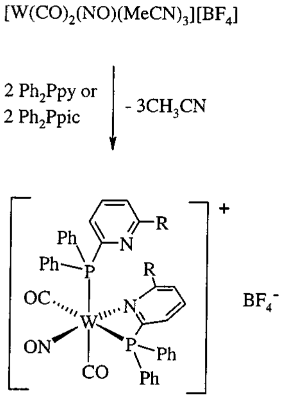
obtained by using $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$[20] as the starting material. Thus, the addition of two equivalents of Ph_2Ppy or Ph_2Ppic to $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ in dichloromethane resulted in substitution of the three acetonitrile ligands by two phosphanes, one of which coordinated in a monodentate fashion and the other in a bidentate mode, thereby affording complexes **9a** and **11**, respectively [Equation (1)]. Spectroscopic studies showed that no further phosphane coordination occurred, even in the presence of an excess of the ligand.



(1)

9a: R = H
11: R = Me

The variable-temperature (VT) NMR spectra of compound **9a** reveal dynamic behaviour. At room temperature, two broad resonances are observed in the ^{31}P-NMR spectrum at $\delta = 24.8$ and $\delta = -18.3$, which sharpen into two doublets below −15 °C. The energy of activation for the exchange process was estimated to be 57(2) kJ/mol by lineshape analysis. When the pyridyl groups in **9a** are replaced by picolyl groups as in complex **11**, no dynamic behaviour is observed, even at 70 °C. In order to obtain more information regarding the mechanism of the pyridyl exchange process, DFT calculations were performed on the model compound $[W(CO)_2(NO)(H_2Ppy)(\eta^2\text{-}H_2Ppy)]^+$. The energy profile of the exchange reaction, together with a systematic sketch of the reaction coordinate, is presented in Figure 1. The distance d_{N1-W} was allowed to vary from 225 pm to 395 pm; it can be seen that the energy rises smoothly from 0 kJ/mol (the reference value for the ground state) to 62 kJ/mol (the transition state) and then decreases again (see Figure 1, solid line).

More interesting still are the changes in d_{N2-W} as a function of the value of d_{N1-W} (Figure 1, dashed line). We analysed this by following the actual linear transit mode, i.e. by bringing the uncoordinated atom N1 in towards the distance for binding to the metal centre. As the N1 atom approaches (d_{N1-W} in the range from 395 pm to 325 pm), the four-membered metallacycle remains essentially intact and d_{N2-W} does not change significantly. At the transition state, two equally long d_{N-W} distances are present. If N1 is now brought closer to the metal centre, d_{N2-W} immediately takes on values around 380 pm, the distance corresponding to the uncoordinated ring. From this, it might be concluded that bond cleavage and bond formation do not occur in a concerted fashion and one may envisage the exchange process as follows. The N2 atom of the free pyridyl unit first approaches the metal centre, which requires about two-thirds of the energy of activation. Bond cleavage then occurs, and in the transition state the two N atoms are only weakly coordinated to the tungsten centre. The formerly bound pyridyl unit rotates away to relieve steric hindrance, allowing formation of the bond between N2 and W. The calculated activation energy of 62 kJ/mol is in good agreement with the experimentally determined value of 57(2) kJ/mol. This result can thus be taken as strong evidence in favour of the suggested reaction mechanism.

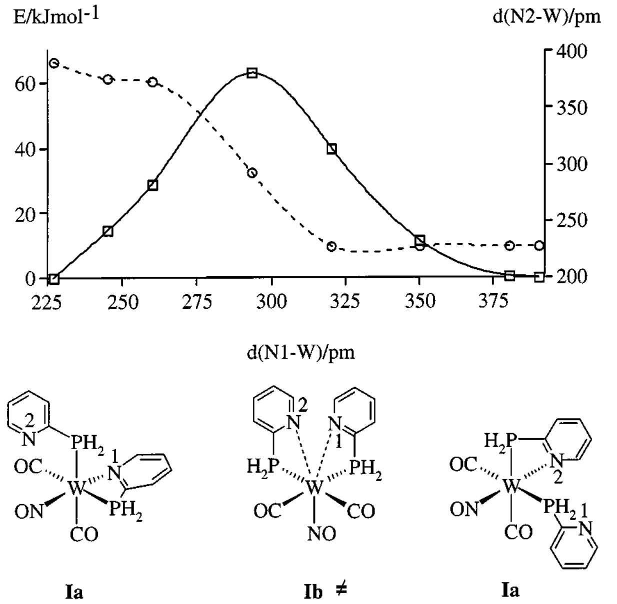
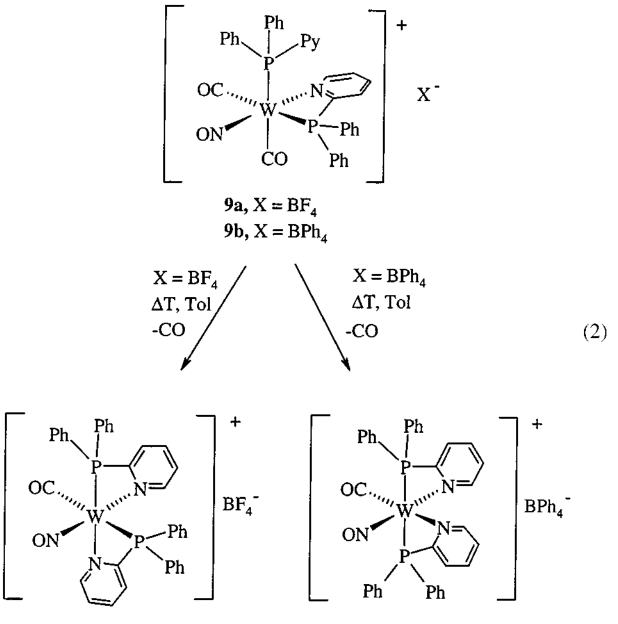


Figure 1. Energy profile for the pyridyl exchange reaction; the solid line refers to the left ordinate axis, the dashed line to the right ordinate axis

Furthermore, it is noteworthy that the two pyridyl groups in complex **11** do not exchange. Taking the geometry of the transition state for **9**, replacing the H atoms in the positions α to N by methyl groups, and assuming a C−C bond length of 153 pm, it can be calculated that the two CH_3 carbon centres are separated by just 213 pm. This is within the range of the effective van der Waals radius of a methyl group (200 pm). It seems likely that the transition-state geometry of the intramolecular rearrangement of **11** does not allow the two pyridyl rings to pass each other. Thus, the exchange process is hindered for steric reasons.

When a solution of **9a** in chloroform was set aside for several hours at room temperature, the formation of small amounts of decarbonylated complex isomers with both phosphane ligands coordinated in a bidentate fashion was observed. On warming the solution to 70 °C, however, decomposition was observed by NMR spectroscopy. In order to confirm the structures of the isomers, a specific synthesis was developed [Equation (2)]. The monocarbonyl complex **20** with the phosphorus donors coordinated in a *cis* arrangement was prepared by heating a suspension of **9b** in toluene to 100 °C with slow removal of the solvent under slightly reduced pressure. A similar procedure was employed to synthesize the *trans* isomer **21**. In order to increase the solubility of the cationic species, it was necessary to replace the BF_4 anion of **9a** by BPh_4, thereby affording the analogous complex **9b**. Dissolution of **9b** with a few drops of acetonitrile in toluene, heating to 95 °C, removal of the solvent under reduced pressure, and repeating of this procedure afforded a red powder. Recrystallization from dichloromethane at −30 °C gave **21** as dark-red crystals. The ^{31}P-NMR spectrum of the product featured an AB system ($^2J_{AB}$ = 121 Hz) along with the respective tungsten satellites and characteristic J_{PW} values of 277 Hz and 299 Hz for the two P atoms located in *trans* positions.



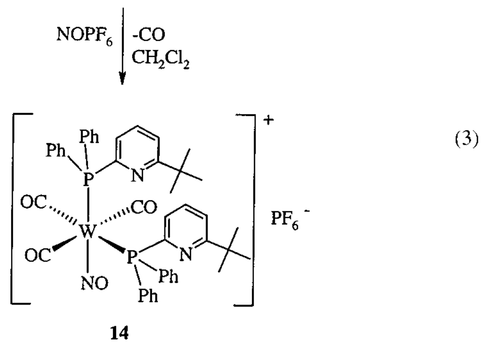
9a, X = BF_4
9b, X = BPh_4

20 **21**

(2)

A suitable reaction for preparing the cationic complex **14** bearing the bulky Ph_2P-*tert*-Bupy ligands that avoided coordination of the pyridine substituents, was found to be nitrosylation of the neutral tetracarbonyl compound **12**, Equation (3).

$W(CO)_4(Ph_2P\text{-}tert\text{-}Bupy)_2$
13



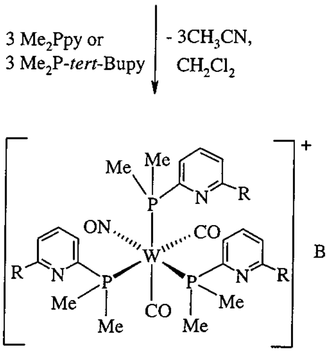
14

(3)

A 20% excess of $NOPF_6$ was found to be essential to achieve complete transformation of **13**. The crude product consisted of **14** (70%) and unidentified impurities (ca. 25%), as well as uncoordinated phosphane (5%). The collected solid was washed several times with diethyl ether and then taken up in a mixture of diethyl ether/dichloromethane. Slow evaporation of the solvents afforded bright-yellow crystals of the desired product.

In contrast, the reaction of the more basic phosphanes Me_2Ppy or Me_2P-*tert*-Bupy with $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ in dichloromethane resulted in the substitution of three acetonitrile ligands by *P*-coordinated phosphanes [Equation (4)]. The formation of the trisubstituted complexes **16** and **18** could be observed by ^{31}P-NMR spectroscopy even after the addition of just one equivalent of the phosphane ligand to the acetonitrile complex.

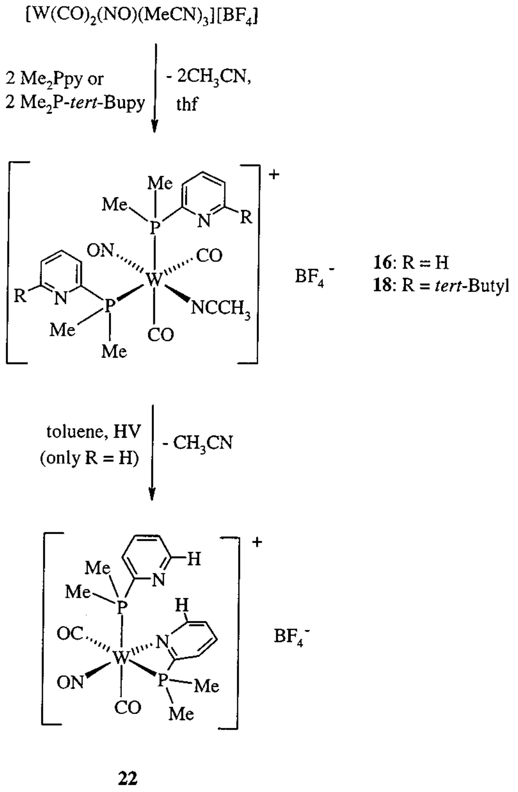
$[W(CO)_2(NO)(MeCN)_3][BF_4]$



16: R = H
18: R = *tert*-Butyl

(4)

Complexes **16** and **18** were found to be very stable in air in the solid state, and only slightly moisture-sensitive in solution. When the former reaction was carried out in THF using exactly two equivalents of the phosphane, the ^{31}P-NMR spectra of the reaction mixtures showed one singlet with a J_{PW} of 254 Hz for the Me_2Ppy derivative and 257 Hz for the Me_2P-*tert*-Bupy derivative, indicating a *cis* arrangement of the two phosphanes coordinated to the tungsten centre. A further resonance of lower intensity was observed in each case, which disappeared upon addition of acetonitrile to the THF solution [Equation (5)]. Removal of the solvents in vacuo (10^{-1} mbar) afforded complex **22** with one Me_2Ppy ligand coordinated to the metal centre in a monodentate fashion and the second coordinated in a bidentate fashion, akin to the situation in complexes **9a** and **11**. With Me_2P-*tert*-Bupy ligands, however, the sterically demanding *tert*-butyl substituent prevents coordination of the pyridine ring and so complex **23a**, with one acetonitrile ligand remaining coordinated to the metal centre, is formed. In contrast to the complexes bearing less bulky phosphanes, the remaining acetonitrile ligand could not be removed from the metal coordination sphere, even at elevated temperatures. Exchange of the BF_4 anion by the more inert tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) **23b** and subsequent heating in vacuo (10^{-4} mbar) led only to slow decomposition of the complex.

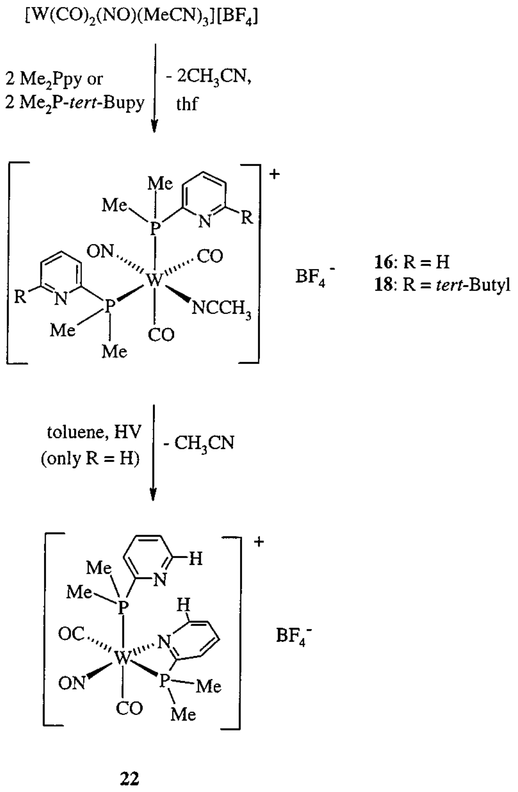


(5)

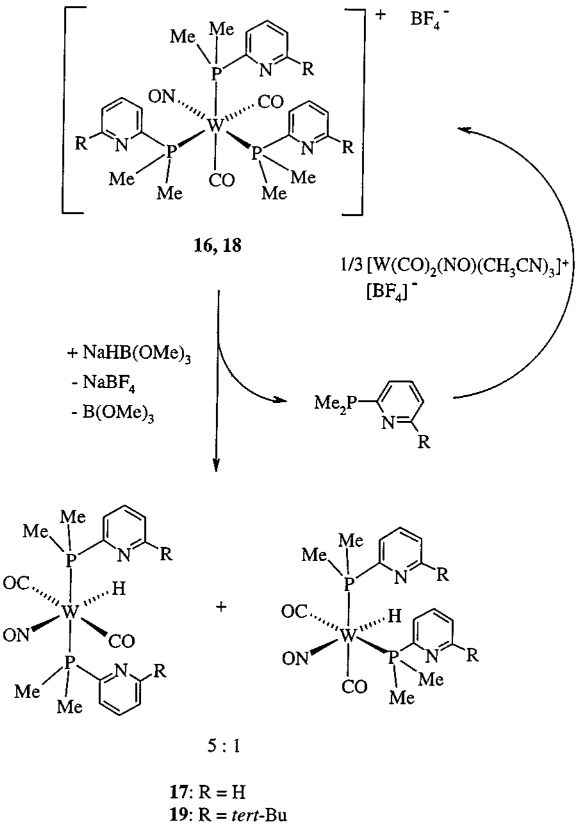
Preparation of the Tungsten Hydrides

Depending on the nature of the cationic nitrosyltungsten complexes, three different hydride reagents were used to obtain the corresponding tungsten hydride compounds. For the cationic complexes **9a** and **11**, which have pyridine substituents coordinated at their metal centres, sodium bis(2-methoxyethyloxy)aluminium hydride (RedAl) was found to give the best yields, whereas for complex **14** sodium tetrahydroborate proved to be most efficient in displacing the carbonyl ligand. The resulting tungsten hydride complexes **10**, **12**, and **15** bearing diphenyl-substituted phosphanes were readily precipitated by rapid addition of ethanol to the reaction mixtures. The *tert*-butyl-substituted derivative **15** was found to be slightly more soluble than **10** and **12** and therefore had to be precipitated at low temperature to prevent further reaction of the hydride with the alcohol [Equation (6)].

Sodium hydrotrimethoxyborate was chosen for the reactions with the trisubstituted phosphane cations **16** and **18**, which afforded the tungsten hydride complexes **17** and **19**. The phosphane ligands abstracted during these reactions could not easily be removed from the products due to similar solubility properties. However, in both cases [W(CH$_3$CN)$_3$(CO)$_2$(NO)][BF$_4$] proved to be an efficient phosphane scavanger affording the cationic starting complex, from which the product could simply be separated by extraction with pentane [Equation (7)].



(6)



(7)

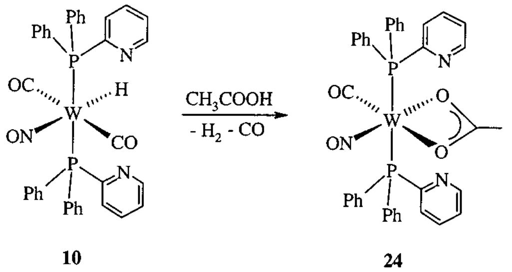
Reactivity Studies

In order to assess the influence of the pyridyl substituents, complexes **10** and **12** were compared with the analogous compound *trans*-$HW(CO)_2(NO)(PPh_3)_2$ prepared by Hillhouse.[21] The NMR chemical shifts and coupling constants of the carbonyl and hydride resonances, as well as the IR stretching vibrations for NO and CO, were found to be essentially identical for the three hydride complexes. Therefore, one can also expect a similar hydridic behaviour, as discussed previously by Berke et al.[22,23] for related compounds.

The reaction of **10** with HI (0.75 M in $CHCl_3$) led to the immediate evolution of hydrogen affording *trans*-$IW(CO)_2(NO)(PPh_2py)_2$ (**25**) [Equation (8)], as described for the PPh_3 derivative.

$$\begin{array}{c} \textit{trans,trans}\text{-}HW(CO)_2(NO)(Ph_2Ppy)_2 + HI \\ \mathbf{10} \\ \Big\downarrow -H_2 \\ \textit{trans,trans}\text{-}IW(CO)_2(NO)(Ph_2Ppy)_2 \\ \mathbf{25} \end{array} \qquad (8)$$

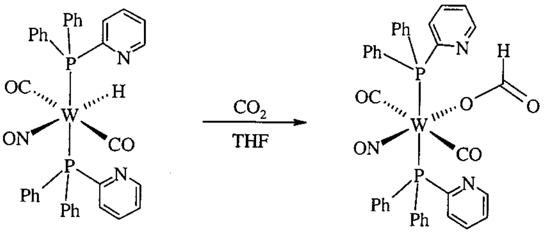
Hydrogen was also evolved when **10** was treated with glacial acetic acid in a mixture of dichloromethane and 2-propanol. Subsequent loss of one carbonyl ligand resulted in the formation of a four-membered metallacycle with the formula *trans*-$W(CO)(NO)(Ph_2Ppy)_2(\eta^2\text{-}CH_3CO_2)$ (**24**) [Equation (9)].



10 **24** (9)

The same decarbonylation reaction was also observed by Hillhouse and afforded the analogous complex bearing PPh_3 ligands.

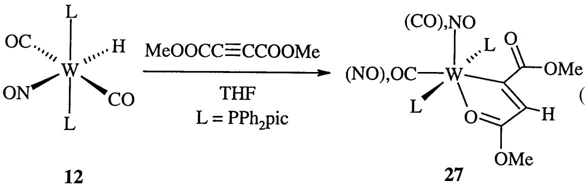
The insertion of carbon dioxide into the metal hydride bond yielding the formato complex **26** was achieved by slowly bubbling a stream of CO_2 gas through a solution of **10** in THF [Equation (10)].



10 **26** (10)

The ^1H-NMR resonance of the formate proton in **26** appears at $\delta = 7.06$ ($\delta = 7.08$ for the PPh_3 derivative). The oxo carbonyl resonance is seen at $\delta = 166.4$ in the ^{13}C-NMR spectrum. Identical shifts have been observed for other phosphane complexes incorporating monodentate formate ligands prepared in our laboratory, such as the analogous $P(OiPr)_3$ derivative.[24] The carbonyl intensity patterns [2050 (w), 1962 (s) cm^{-1}] in the infrared spectra are characteristic of a *trans*-dicarbonyl geometry by analogy with the PPh_3 derivative.

A further insertion experiment was performed by treating **12** with dimethyl acetylenedicarboxylate in THF. The resulting IR spectrum featured one carbonyl band at 1935 cm^{-1} indicating the loss of a single carbonyl ligand. The ^1H- and ^{13}C-NMR data of the resulting complex **27** were compared with those of the PMe_3 derivative.[22] However, it could not be unambiguously established which of the two isomers with regard to the positions of the NO and CO ligands had been formed [Equation (11)].

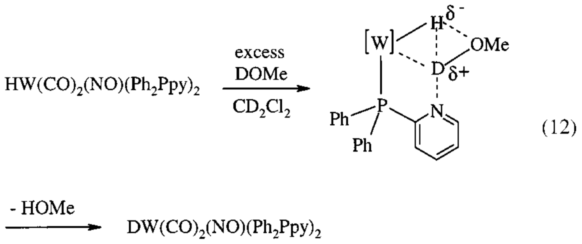


12 **27** (11)

The above reactions displayed approximately the same characteristics irrespective of whether a PPh_2py or a PPh_3 ligand was coordinated to the tungsten centre. According to the spectroscopic data and the reactivities of the tungsten hydride complexes, the pyridyl substituents seemingly have no influence on the electronic character of the hydride ligand.

Nevertheless, an H/D exchange experiment was performed in order to assess whether the basic pyridine N atom had any effect on the reactivities of the hydride complexes. The interaction of a protic alcohol function with the pyridyl substituents located in the ligand sphere could facilitate proton transfer to the hydride. In order to compare the H/D exchange rates of $HW(CO)_2(NO)(PPh_3)_2$ and $HW(CO)_2(NO)(PPh_2py)_2$ (**10**) with [D_4]methanol, a 1:1 mixture of the two complexes in CD_2Cl_2 was prepared and then a 150-fold excess of [D_4]methanol was added at 0 °C. Higher temperatures (+5 °C) led to rapid decomposition of the complexes with evolution of HD. By monitoring the reaction by ^1H-NMR spectroscopy for 25 min at 0 °C, it was observed that the hydride resonance of **9** at $\delta = -0.07$ completely disappeared while in the $^{31}P\{^1H\}$-NMR spectra a triplet due to deuterated **9** with a PD coupling constant of $J = 3$ Hz appeared. In contrast, the analogous resonances due to $HW(CO)_2(NO)(PPh_3)_2$ did not change. After 22 hours, **10** had been completely consumed while only 30% of the PPh_3 complex had been transformed to the deuteride with partial decomposition through ligand abstraction [Equation (12)]. After a reaction time of one hour under the same conditions and further addition of [D_1]methanol to the mixture, the deuteride complex **28** readily precipitated and could be fully characterized.

Although no spectroscopic evidence was found to support the concerted mechanism proposed in Equation (12), it could be concluded from these experiments that the interaction of the protic alcohol with the pyridyl substituent is responsible for the accelerated H/D exchange.



28

We also carried out exploratory catalytic experiments with the hydride complexes **10** and **19** in order to investigate their activities in the ionic hydrogenation of imines. This type of catalysis has been reported for a variety of Ru, Ir, Rh, and Ti complexes. With compound **10**, we obtained the most promising results when a 5:1 mixture of isopropylisopropylideneamine and its corresponding BPh_4 salt were dissolved in a 2:1 mixture of THF/CH_2Cl_2. The amount of tungsten hydride catalyst used was 10 mol-% with respect to the imine. Stirring the reaction mixture at 70 °C for 14 hours under 60 atm of hydrogen resulted in the conversion of 35% of the imine and iminium salt to the corresponding amine and ammonium salt, respectively. The ^{31}P-NMR spectra showed one resonance corresponding to the free phosphane ligand. We conclude that about 3−4 turnovers were reached before decomposition of the catalyst occurred. Addition of the BPh_4 salt was found to be essential to initiate the reaction; no hydrogenation was observed if only the pure imine was present in solution.

When the same experiment was performed using **19** as the catalyst, an additional product could be observed in the ^{1}H-NMR spectrum. Reference spectra and GC-MS analysis confirmed the formation of both mono- and diisopropylamine. Further investigations using hydrogen pressures up to 100 atm and temperatures up to 90 °C led to changes in the isopropylamine/diisopropylamine ratio from 1:2 (60 °C/60 atm) up to 3:1 (90 °C/100 atm). The mechanisms of these reactions have not yet been clarified and are currently under investigation in our laboratory.

X-ray Crystal Structure Determinations

The following complexes were characterized by X-ray analysis: *cis,cis*-[W(CO)$_2$(NO)(Ph$_2$Ppy)(η^2-Ph$_2$Ppy)][BF$_4$] (**9a**), *cis,cis*-[W(CO)$_2$(NO)(Ph$_2$Ppic)(η^2-Ph$_2$Ppic)][BF$_4$] (**11**), *cis,mer*-[W(CO)$_3$(NO)(Ph$_2$P-*tert*-Bupy)$_2$][PF$_6$] (**14**), and *cis,cis*-[W(CO)(NO)(η^2-Ph$_2$Ppy)$_2$][BF$_4$] (**20**). In the Figures the anions of all the structures have been omitted for the sake of clarity.

Compounds **9a** (Figure 2) and **11** (Figure 3) show strongly distorted octahedra due to the formation of the four-membered metallacycle with P−W−N bond angles of approximately 64.5° in each case. The W−N(pyridyl) bond length in **11** is only slightly lengthened to 2.259(5) Å compared to 2.240 Å in **9a**. However, the steric influence of the methyl substituent in **11** is clearly apparent from the opening of the corresponding equatorial bond angles, N(1)−W(1)−C(36) in **9a** and N(2)−W(1)−C(1) in **11**, from 94.12° to 101.4(2)°.

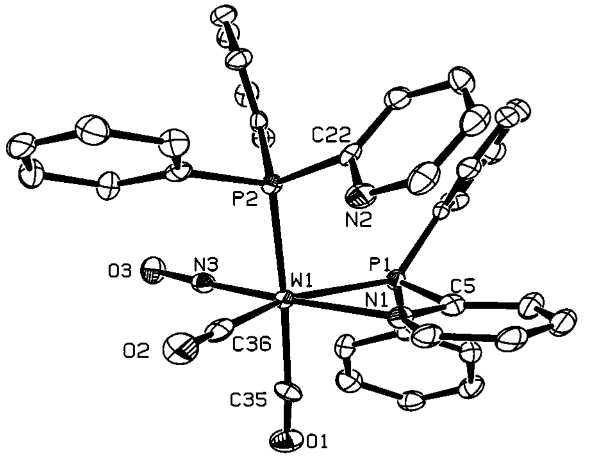


Figure 2. View of the structure of the cation of **9a**; selected bond lengths (Å) and angles (°): W(1)−N(1) 2.240, W(1)−P(1) 2.537, W(1)−P(2) 2.536, W(1)−C(36) 2.046, W(1)−N(3) 1.809, W(1)−C(35) 2.051; N(3)−W1−C(36) 95.11, N(3)−W1−C(35) 92.08, N(3)−W1−N(1) 170.70, N(3)−W1−P(2) 87.89, N(3)−W1−P(1) 106.24, C(36)−W1−C(35) 89.41, C(36)−W1−N(1) 94.12, C(36)−W1−P(2) 86.15, C(35)−W1−N(1) 86.95, C(35)−W1−P(1) 86.70, N(1)−W1−P(2) 93.80, N(1)−W1−P(1) 64.48, P(2)−W1−P(1) 97.59

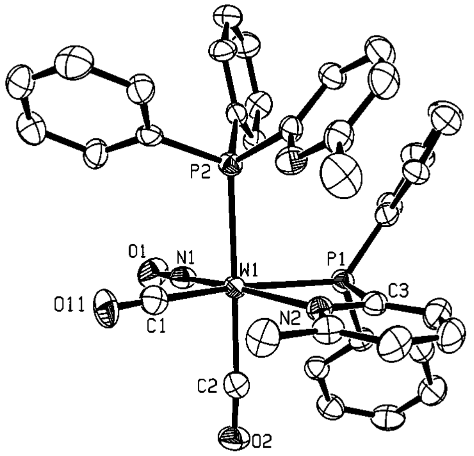


Figure 3. View of the structure of the cation of **11**; selected bond lengths (Å) and angles (°): W(1)−N(2) 2.259(5), W(1)−P(1) 2.539(2), W(1)−P(2) 2.564(1), W(1)−C(1) 2.046(7), W(1)−N(1) 1.810(5), W(1)−C(2) 2.047(6); P(1)−W(1)−P(2) 94.08(5), P(1)−W(1)−N(1) 104.1(2), P(2)−W(1)−N(1) 91.5(2), P(1)−W(1)−N(2) 64.5(1), P(2)−W(1)−N(2) 94.8(1), N(1)−W(1)−N(2) 167.3(2), P(2)−W(1)−C(1) 87.9(2), N(1)−W(1)−C(1) 89.8(2), N(2)−W(1)−C(1) 101.4(2), P(1)−W(1)−C(2) 88.2(2), N(1)−W(1)−C(2) 90.9(2), N(2)−W(1)−C(2) 83.4(2), C(1)−W(1)−C(2) 89.2(3), W(1)−P(1)−C(3) 83.6(2)

The W−N(pyridyl) bond lengths in the monocarbonyl complex **20** (Figure 4) are 2.258(3) Å for N(2) and 2.210(3) Å for N(1). The longer W−N(2) bond length can be attributed to the strong *trans* influence of the nitrosyl ligand. This effect is also manifested in the bond angles in the less strained metallacycle, 65.50(9)° for N(2)−W(1)−C(2) [cf. 64.12(9)° for N(1)−W(1)−C(1)].

In compound **14** (Figure 5), the *trans* influence of the nitrosyl ligand is also reflected in the longer phosphorus−tungsten bond length, which is 2.640(2) Å for W(1)−P(30), as compared to 2.591(2) Å for W(1)−P(10) with a carbonyl ligand coordinated in a *trans* orientation.

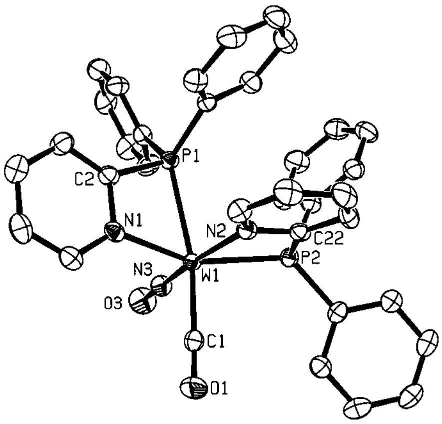


Figure 4. View of the structure of the cation of **20**; selected bond lengths (Å) and angles (°): W(1)−P(10) 2.591(2), W(1)−P(30) 2.640(2), W(1)−N(4) 1.896(7), W(1)−C(1) 1.977(8), W(1)−C(2) 2.080(9), W(1)−C(3) 2.06(1); P(1)−W(1)−P(2) 98.41(3), P(1)−W(1)−N(1) 64.12(9), P(2)−W(1)−N(1) 152.51(9), P(1)−W(1)−N(2) 84.40(8), P(2)−W(1)−N(2) 65.50(9), N(1)−W(1)−N(2) 90.7(1), P(1)−W(1)−N(3) 96.7(1), P(2)−W(1)−N(3) 105.3(1), N(1)−W(1)−N(3) 98.0(1), P(2)−W(1)−C(1) 95.0(1), N(1)−W(1)−C(1) 99.1(1), N(2)−W(1)−C(1) 90.9(1), N(3)−W(1)−C(1) 90.7(2), W(1)−P(1)−C(2) 82.5(1), W(1)−P(2)−C(22) 84.6(1), W(1)−N(1)−C(2) 108.9(3), W(1)−N(2)−C(22) 104.4(2)

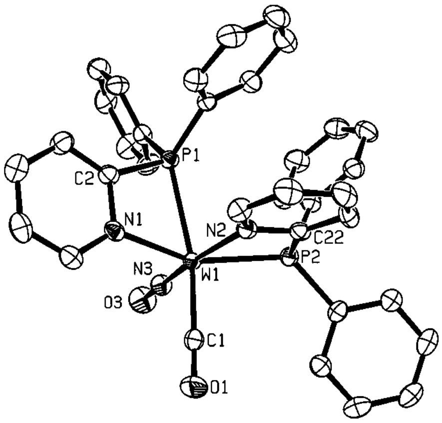


Figure 5. View of the structure of the cation of **14**; selected bond lengths (Å) and angles (°): W(1)−P(10) 2.591(2), W(1)−P(30) 2.640(2), W(1)−N(4) 1.896(7), W(1)−C(1) 1.977(8), W(1)−C(2) 2.080(9), W(1)−C(3) 2.06(1); P(10)−W(1)−P(30) 104.39(6), P(10)−W(1)−N(4) 82.0(2), P(30)−W(1)−C(1) 86.7(2), N(4)−W(1)−C(1) 87.3(3), P(10)−W(1)−C(2) 91.2(2), P(30)−W(1)−C(2) 82.5(2), N(4)−W(1)−C(2) 91.7(3), C(1)−W(1)−C(2) 93.0(3), P(10)−W(1)−C(3) 87.0(2), P(30)−W(1)−C(3) 91.5(2), N(4)−W(1)−C(3) 94.7(3), C(1)−W(1)−C(3) 90.0(4), W(1)−P(10)−C(4) 113.3(3), W(1)−P(10)−C(13) 108.3(2), W(1)−P(10)−C(19) 121.5(3), W(1)−P(30)−C(34) 108.3(2), W(1)−P(30)−C(43) 114.7(3), W(1)−P(30)−C(49) 118.3(2)

Experimental Section

General Techniques: All preparations were carried out under dry nitrogen using conventional Schlenk or glove-box techniques and dry, air-free solvents. − IR spectra were recorded with a Bio-Rad FTS-45 instrument. − ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded with a Varian Gemini 200 (200 MHz for ^{1}H, 50.3 MHz for ^{13}C), a Varian Gemini 300 (300 MHz for ^{1}H, 121.5 MHz for ^{31}P, 75.4 MHz for ^{13}C), or a Bruker Avance 500 (125.8 MHz for ^{13}C). All ^{31}P-NMR spectra were proton-decoupled. The spectra were simulated using the program gNMR 4.1 (Cherwell Scientific) in the automatic iteration mode. Sodium bis(2-methoxyethyloxy)aluminium hydride (RedAl, 3.5 M in toluene) was purchased from Aldrich Chemical Co.

Sodium 3,3-Dimethyl-2-oxobutoxide (1): Sodium ribbon (15.2 g, 0.66 mol) was added to 350 mL of dry diethyl ether. A mixture of ethyl formate (48.9 g, 0.66 mol) and pinacoline (66.1 g, 0.66 mol) was then added dropwise to the reaction mixture over a period of 2 h at −30 °C. When the addition was complete, the solution was allowed to warm to room temperature and stirring was continued for a further 1 h. After evaporation of the solvent, the residual brown slurry was washed with small amounts of diethyl ether and hexane. The crude product was used in the next step without further purification. Yield: 92.4 g (0.55 mol, 83%).

6-*tert*-Butyl-3-cyano-2-pyridone (2): Sodium salt **1** (92.4 g, 0.55 mol) and cyanoacetamide (46.25 g, 0.55 mol) were dissolved in water (200 mL). Meanwhile, a solution consisting of glacial acetic acid (8 mL) and water (20 mL) was adjusted to pH = 8 by the addition of piperidine. The two solutions were then mixed and the mixture was refluxed for 2 h, cooled, and acidified with glacial acetic acid. After filtration, the brown residue was washed with water (200 mL), taken up in ethanol (200 mL), and the resulting solution was treated with activated charcoal (5 g). Evaporation of the solvent in vacuo gave the product as a white powder. Yield: 22 g (0.125 mol, 23%); m.p. 194 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 12.59$ (br., 1 H), 7.81 (d, $^{3}J_{HH} = 7.7$ Hz, 1 H), 6.26 (d, $^{3}J_{HH} = 7.7$ Hz, 1 H), 1.41 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR (200 MHz, $CDCl_3$): $\delta =$ 164.3 (s), 162.6 (s), 148.4 (s, CH), 115.6 (s), 102.2 (s, CH), 35.9 (s, CMe_3), 28.7 [s, $C(CH_3)_3$]. − MS (EI); *m/z* (%): 176 [M^+] (22), 161 [$M^+ - CH_3$] (100), 134 [$M^+ - CH_3 - CN - H$] (12). − $C_{10}H_{12}N_2O$ (176.22): calcd. C 68.16, H 6.86, N 15.90; found C 67.89, H 6.47, N 15.82.

6-*tert*-Butyl-2-oxo-3-pyridinecarboxylic Acid (3): A solution of **2** (20.0 g, 0.11 mol) in concentrated hydrochloric acid (200 mL) was refluxed for 5 h, poured onto 200 g of ice, and washed several times with cold water. Evaporation of the water in vacuo gave the product as a white solid. Yield: 18.76 g (96 mmol, 84%); m.p. 240 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 13.80$ (br., 1 H), 12.40 (br., 1 H), 8.54 (d, $^{3}J_{HH} = 8$ Hz, 1 H), 6.61 (d, $^{3}J_{HH} = 8$ Hz, 1 H), 1.46 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 166.1$ (s), 165.4 (s), 164.0 (s), 148.1 (s, CH), 115.6 (s), 106.0 (s, CH), 36.4 (s, CMe_3), 29.3 [s, $C(CH_3)_3$]. − MS (EI); *m/z* (%) = 194 [M^+] (100), 179 [$M^+ - CH_3$] (76), 177 [$M^+ - OH$], 162 [$M^+ - CH_3 - OH$] (100). − $C_{10}H_{13}NO_3$: calcd. C 61.53, H 6.71, N 7.17; found C 61.96, H 6.30, N 7.33.

6-*tert*-Butyl-2-pyridol (4): In a 500-mL flask fitted with a cold finger, **3** (18.0 g, 92.3 mol) was heated to 315 °C for 20 min by means of a molten-metal bath. When the evolution of carbon dioxide had ceased, the residual black material was sublimed at 150 °C and a pressure of 0.1 mbar. The product was obtained in the form of white crystals. Yield: 9.4 g (62 mmol, 67%); m.p. 141 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 11.76$ (br., 1 H), 7.34 (m, 1 H), 6.40 (m, 1 H), 6.09 (m, 1 H), 1.34 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 165.0$ (s), 157.1 (s), 141.7 (s, CH), 117.3 (s, CH), 101.9 (s, CH), 36.4 (s, CMe_3), 29.3 [s, $C(CH_3)_3$]. − MS (EI); *m/z* (%): 151 [M^+] (100), 136 [$M^+ - CH_3$] (100). − $C_9H_{13}NO$ (151.21): calcd. C 71.49, H 8.67, N 9.26; found C 71.26, H 8.48, N 9.33.

2-*tert*-Butyl-6-chloropyridine (5): To a solution of **4** (9.0 g, 59.6 mmol) in refluxing phosphorus oxychloride (10 mL), phosphorus pentachloride (13.8 g) was added in small portions over a period of 30 min. The bath temperature was then increased to 160

°C and maintained at this temperature for 1 h. After cooling the mixture to room temperature and removing the solvent under reduced pressure, the residue was poured onto ice. The resulting black mixture was made strongly basic with sodium hydroxide and steam distilled to afford a pale oil. The crude product was taken up in diethyl ether and dried with Na_2SO_4. Removal of the solvent and distillation of the oil (b.p. 47 °C, 1 mbar) afforded a colourless liquid. Yield: 5.4 g (32.3 mmol, 48%), − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55 (m, 1 H, py), 7.22 (m, 1 H, py), 7.10 (m, 1 H, py), 1.35 [s, 9 H, $C(CH_3)_3$]. − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 170.6 (s, α-C, py), 150.2 (s, α-C, py), 138.7 (s, py), 121.1 (s, py), 117.4 (s, py), 37.5 (s, *C*Me₃), 29.9 [s, $C(CH_3)_3$]. − MS (EI); *m/z* (%): 169 [M^+] (88), 154 [$M^+ - CH_3$] (100). − $C_9H_{12}NCl$ (169.66): calcd. C 63.72, H 7.13, N 8.26; found C 63.94, H 7.08, N 8.18.

2-(6-*tert*-Butylpyridyl)diphenylphosphane (6): To a solution of diphenylphosphane (2.75 g, 14.8 mmol) in THF (50 mL) at room temperature, 1.6 M *n*BuLi in THF (9.25 mL, 14.8 mmol) was added dropwise over a period of 30 min. The resulting red solution was stirred for a further 30 min and then a solution of **5** (2.5 g, 14.7 mmol) in THF (10 mL) was slowly added. The reaction mixture was stirred for a further 14 h, then quenched with ethanol (15 mL), and the solvents were evaporated under reduced pressure. The resulting pale-yellow solid was redissolved in hexane (200 mL) and this solution was treated with activated charcoal (5 g). After filtration and evaporation of the solvent, white crystals were obtained. Yield: 3.0 g (9.46 mmol, 64%). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51−7.35 (m, 10 H, Ph; 1 H, py), 7.21 (m, 1 H, py), 6.97 (m, 1 H, py), 1.34 (s, 9 H, *t*Bu). − ^{31}P NMR (300 MHz, $CDCl_3$): δ = −3.4 (s). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 169.3 (d, $^1J_{CP}$ = 10 Hz, *ipso*-py), 161.6 (d, $^3J_{CP}$ = 5 Hz, *ipso*-py), 137.1 (d, $^1J_{CP}$ = 9 Hz, *ipso*-Ph), 135.6 (d, J_{CP} = 4 Hz, py), 134.2 (d, J_{CP} = 20 Hz, Ph), 128.6 (s, Ph), 128.2 (d, J_{CP} = 7 Hz, Ph), 125.0 (d, *J* = 20 Hz, py), 117.3 (s, py). − MS (FAB); *m/z* (%): 319 [M^+] (95), 185 [M^+ − *tert*-Bupy] (10). − $C_{21}H_{22}NP$ (319.39): calcd. C 78.97, H 6.94, N 4.39; found C 78.74, H 6.73, N 4.21.

2-(6-*tert*-Butylpyridyl)dimethylphosphane (7): To a solution of tetramethyldiphosphane (4.4 g, 36 mmol) in THF (300 mL) was added potassium metal (2.82 g, 72.1 mmol). The mixture was stirred for 1 day at 35 °C and then the unchanged potassium metal was removed. To the yellow solution of potassium dimethylphosphide was added **5** (12.1 g, 71.3 mmol). The resulting dark-red solution was stirred for 2 h, the solvent was evaporated in vacuo, and the residue was extracted with diethyl ether (3 × 50 mL). The combined dark-red extracts were distilled under reduced pressure (b.p. 62−72 °C, 0.1 mbar) to give a colourless oil (9.4 g), which proved to be an azeotropic mixture of **7** and unchanged 2-*tert*-butyl-6-chloropyridine. The ratio of the mixture was estimated from the ^1H-NMR spectrum to be 3:2. − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45 (m, py, 2 H), 7.15 (m, py, 1 H), 1.36 [d, 6 H, $^2J_{PH}$ = 2.2 Hz, $(CH_3)_2P$], 1.35 (s, 9 H, *t*Bu). − ^{31}P NMR (300 MHz, $CDCl_3$): δ = −40.6 (s).

2-(6-Methylpyridyl)diphenylphosphane (8): To a solution of diphenylphosphane (3.68 g, 19.8 mmol) in THF (70 mL) at room temperature, 1.6 M *n*-butyllithium (12.4 mL, 20.2 mmol) was added over a period of 30 min. After stirring for a further 30 min at room temperature, the red reaction mixture was cooled to 0 °C and a solution of 6-chloro-2-picoline (2.53 g, 19.8 mmol) in THF (20 mL) was added dropwise. Further stirring for 3 h at room temperature and subsequent addition of ethanol (20 mL) gave a pale-yellow solution. The solvent was evaporated under reduced pressure and the residue was extracted with hexane (400 mL). After filtration through Celite and crystallization at −30 °C, the product was obtained as large white needles. Yield: 460 mg (0.294 mmol, 77%). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44 (m, 1 H, py), 7.37 (m, 10 H, Ph), 7.05 (m, 1 H, py), 6.83 (m, 1 H, py), 2.58 (s, 3 H, CH_3). − ^{31}P NMR (300 MHz, $CDCl_3$): δ = −4.4 (s). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 162.9 (d, $^3J_{CP}$ = 7 Hz, *ipso*-py), 158.9 (d, $^1J_{CP}$ = 15 Hz, *ipso*-py), 136.5 (d, $^1J_{CP}$ = 15 Hz, *ipso*-Ph), 135.8 (d, J_{CP} = 2 Hz, py), 134.0 (d, J_{CP} = 20 Hz, Ph), 128.8 (s, Ph), 128.4 (d, J_{CP} = 7 Hz, Ph), 124.8 (d, *J* = 11 Hz, py), 121.9 (s, py), 24.6 (s, CH_3). − MS (EI); *m/z* (%): 277 [M^+] (100), 200 [M^+ − Ph] (30), 185 [$M^+ - Ph - CH_3$] (12). − $C_{18}H_{16}NP$ (277.31): calcd. C 77.96, H 5.82, N 5.05; found C 78.31, H 5.56, N 4.97.

***cis*,*cis*-[W(CO)₂(NO)(Ph₂Ppy)(η²-Ph₂Ppy)][BF₄] (9a):** To a solution of $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ (1.5 g, 3.13 mmol) in dichloromethane was added tris(2-pyridyl)phosphane (1.65 g, 6.27 mmol). After stirring the reaction mixture for 1 h at room temperature, it was concentrated to a volume of 7 mL in vacuo and diethyl ether (5 mL) was slowly added, which induced the formation of a dark-yellow oil. The residue was dissolved in dichloromethane and diethyl ether (10 mL) was again slowly added, which led to the deposition of a yellow solid. The precipitate was filtered off and washed with diethyl ether (2 × 10 mL) to give **9a** as a yellow powder. Yield: 2.2 g (2.49 mmol, 80%). − ^1H NMR (200 MHz, −30 °C, CD_2Cl_2): δ = 8.51−7.55 (m, Ph + py). − ^{31}P NMR (300 MHz, −30 °C, CD_2Cl_2): δ = −25.1 (d, $^2J_{PP}$ = 22 Hz, J_{PW} = 267 Hz), −18.6 (d, $^2J_{PP}$ = 22 Hz, J_{PW} = 220 Hz). − ^{13}C NMR (300 MHz, −30 °C, CD_2Cl_2): δ = 213.0 (dd, $^2J_{CP}$ = 5 × 36 Hz, CO), 207.9 (dd, $^2J_{CP}$ = 6 × 42 Hz, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2037 cm^{-1} (s), 1966 (s), 1676 (m). − MS (FAB); *m/z* (%): 796 [M^+] (80), 768 [M^+ − CO] (75). − $C_{36}H_{28}BF_4N_3O_3P_2W$ (883.24): calcd. C 48.96, H 3.20, N 4.76; found C 48.78, H 3.02, N 4.51.

***cis*,*cis*-[W(CO)₂(NO)(Ph₂Ppy)(η²-Ph₂Ppy)][BPh₄] (9b):** A mixture of **9a** (300 mg, 0.34 mmol) and sodium tetraphenylborate (116 mg, 0.34 mmol) was stirred in THF (8 mL) for 30 min and then filtered through Celite. After removing the solvent in vacuo, the yellow oil was taken up in dichloromethane and filtered through a small pad of silica gel. The filtrate was then concentrated to a volume of 1 mL in vacuo and diethyl ether (4 mL) was added to precipitate the product as a yellow solid. The collected product was washed with pentane (3 × 5 mL) and recrystallized from CH_2Cl_2/Et_2O to give yellow crystals. Yield: 300 mg (0.25 mmol, 73%). − ^1H NMR (300 MHz, −30 °C, CD_2Cl_2): δ = 8.25−6.75 (m). − ^{31}P NMR (300 MHz, −30 °C, CD_2Cl_2): δ = 24.8 (d, J_{PP} = 21 Hz, J_{PW} = 267 Hz), −18.3 (d, J_{PP} = 21 Hz, J_{PW} = 219 Hz). − ^{13}C NMR (300 MHz, −30 °C, CD_2Cl_2): δ = 212.9 (dd, $^2J_{CP}$ = 5 × 36 Hz, CO), 207.5 (dd, $^2J_{CP}$ = 6 × 43 Hz, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2037 cm^{-1} (s), 1966 (s), 1677 (m). − MS (FAB-POS): *m/z* (%) = 796 [M^+] (4), 768 [M^+ − CO] (4). − $C_{60}H_{48}BN_3O_3P_2WCH_2Cl_2$ (1200.6): calcd. C 61.04, H 4.20, N 3.50; found C 60.97, H 4.17, N 3.54.

***trans*,*trans*-HW(CO)₂(NO)(Ph₂Ppy)₂ (10):** To a solution of **9a** (340 mg, 0.374 mmol) in THF (25 mL), sodium dihydrobis(2-methoxyethyloxy)aluminate (10.8 mL, 0.035 M in THF) was slowly added at 0 °C. After stirring for 10 min at room temperature, the reaction mixture was concentrated to a volume of 3 mL in vacuo and ethanol (8 mL) was added dropwise to precipitate the product. The mixture was filtered, and the collected yellow solid was sequentially washed with ethanol (2 × 5 mL) and diethyl ether (2 × 3 mL) to give a bright-yellow powder. Yield: 220 mg (0.276 mmol, 74%). − ^1H NMR (300 MHz, C_6D_6): δ = 8.44 (m, 2 H, py), 7.92 (m, 8 H, Ph), 7.64 (m, 2 H, py), 7.08−6.94 (m, 12 H, Ph), 6.84 (m, 2 H, py), 6.39 (m, 2 H, py), 0.62 (t, 1 H, J_{PH} = 22.4 Hz, J_{WH} = 31.1 Hz). − ^{31}P NMR (300 MHz, C_6D_6): δ = 30.3 (s, J_{PW} = 289 Hz). − ^{13}C

NMR (300 MHz, C_6D_6): δ = 217.2 (t, $^2J_{CP}$ = 7 Hz, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1935 cm^{-1} (s), 1689 (m), 1595 (m). − MS (FAB); *m/z* (%): 797 [M^+] (4), 769 [M^+ − CO] (20), 740 [M^+ − 2 CO] (25). − $C_{36}H_{29}N_3O_3P_2W$ (797.45): calcd. C 54.22, H 3.67, N 5.27; found C 53.96, H 3.92, N 5.04.

***cis,cis*-[W(CO)$_2$(NO)(Ph$_2$Ppic)(η^2-Ph$_2$Ppic)][BF$_4$] (11):** To a solution of [W(CH_3CN)$_3$(CO)$_2$(NO)][BF_4] (170 mg, 0.354 mmol) in dichloromethane (5 mL) was added 2-(6-methylpyridyl)diphenylphosphane (196 mg, 0.71 mmol). After stirring for 90 min at room temperature, the reaction mixture was concentrated to a volume of approximately 2.5 mL, whereupon diethyl ether was slowly added. The resulting yellow precipitate was collected by filtration and washed with pentane. The product could be conveniently recrystallized from CH_2Cl_2/Et_2O to give yellow crystals. Yield: 320 mg (249 mmol, 91%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.20−6.70 (m, 26 H, Ph + py), 2.40 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 23.6 (d, $^2J_{PP}$ = 21 Hz, J_{PW} = 269 Hz), −22.8 (d, $^2J_{PP}$ = 21 Hz, J_{PW} = 215 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 211.2 (dd, $^2J_{CP}$ = 7 × 39 Hz, CO), 207.8 (dd, $^2J_{CP}$ = 6 × 42 Hz, CO), 25.4 (s, CH_3), 24.2 (s, CH_3). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2036 cm^{-1} (s), 1967 (s), 1675 (m). − MS (FAB); *m/z* (%): 824 [M^+] (38), 796 [M^+ − CO] (30), 768 [M^+ − 2 CO] (10). − $C_{38}H_{32}BF_4N_3O_3P_2WCH_2Cl_2$ (996.23): calcd. C 47.02, H 3.44, N 4.22; found C 46.83, H 3.15, N 4.42.

***trans,trans*-HW(CO)$_2$(NO)(Ph$_2$Ppic)$_2$ (12):** To a solution of **9** (700 mg, 0.770 mmol) in THF (25 mL), sodium bis(2-methoxyethyloxy)dihydroaluminate (2.2 mL, 0.35 M in THF) was slowly added at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was concentrated to a volume of 2 mL in vacuo, whereupon ethanol (50 mL) was added dropwise to precipitate the product. The mixture was filtered, and the collected yellow solid was sequentially washed with ethanol (2 × 10 mL) and diethyl ether (2 × 10 mL) to give a yellow powder. Yield: 355 mg (0.43 mmol, 56%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.70−7.05 (m, 26 H, Ph + py), 2.55 (s, 6 H, CH_3), −0.06 (t, 1 H, J_{PH} = 24.2 Hz, J_{WH} = 31.6 Hz). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 31.1 (s, J_{PW} = 292 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 215.6 (t, $^2J_{CP}$ = 6 Hz, CO), 24.5 (s, CH_3). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1937 cm^{-1} (s), 1680 (m), 1592 (m). − MS (FAB); *m/z* (%): 826 [M^+] (12), 797 [M^+ − CO − H] (40), 769 [M^+ − 2 CO − H] (25). − $C_{38}H_{33}N_3O_3P_2W$ (825.5): calcd. C 55.29, H 4.03, N 5.09; found C 55.49, H 3.98, N 5.03.

***cis/trans*-W(CO)$_4$(Ph$_2$P-*tert*-Bupy)$_2$ (13):** To a solution of Ph$_2$P-*tert*-Bupy (390 mg, 1.23 mmol) in toluene (12 mL) was added tetracarbonyldi(piperidine)tungsten (280 mg, 0.60 mmol). The resulting yellow suspension was refluxed and stirred for 90 min, in the course of which homogeneity was attained. After filtration through a short pad of silica gel, the solvent was evaporated from the filtrate to afford the product as a mixture of isomers. Yield: 480 mg (0.51 mmol, 86%). The pure *trans* isomer could be isolated by column chromatography. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75−7.15 (m, 26 H, Ph + py), 1.35 [s, 18 H, C(CH_3)$_3$]. − ^{31}P NMR (300 MHz, $CDCl_3$): δ = 29.8 (s, J_{PW} = 284 Hz). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 203.3 (t, *J* = 6 Hz, CO), 38.0 (s, *C*Me$_3$), 30.0 (s, CH_3). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1890 cm^{-1} (s). − MS (FAB); *m/z* (%): 920 [M^+ − CH_3] (18), 850 [M^+ − 3 CO] (4), 821 [M^+ − 4 CO] (6), 503 [M^+ − 4 CO − L] (25). − $C_{46}H_{44}N_2O_4P_2W$ (934.67): calcd. C 59.11, H 4.75, N 3.00; found C 59.09, H 5.05, N 2.93.

[W(CO)$_3$(NO)(Ph$_2$P-*tert*-Bupy)$_2$][PF$_6$] (14): To a solution of **13** (190 mg, 0.203 mmol) in dichloromethane (5 mL) was added NOPF$_6$ (42 mg, 0.24 mmol). The resulting mixture was vigorously stirred, in the course of which it darkened in colour from yellow to green-orange. When the evolution of CO had ceased, a further portion of NOPF$_6$ (8.4 mg) was added and stirring was continued for 15 h. The reaction mixture was then concentrated to a volume of ca. 0.5 mL in vacuo and benzene (6 mL) was added. Concentration of this solution to a volume of 3 mL led to the separation of a green oil. The pale-yellow solution was decanted and the residue was washed with diethyl ether (2 × 4 mL). The crude product was recrystallized from CH_2Cl_2/Et_2O by slow evaporation of the solvent mixture at atmospheric pressure to give bright-yellow crystals. Yield: 109 mg (1.01 mmol, 50%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.75−6.80 (m, 26 H, Ph + py), 1.42 (s, 9 H, CH_3), 1.32 (s, 9 H, CH_3). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 18.7 (d, $^2J_{PP}$ = 22 Hz, J_{PW} = 263 Hz), 12.5 (d, $^2J_{PP}$ = 22 Hz, J_{PW} = 178 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 200.6 (t, $^2J_{CP}$ = 8 Hz, CO), 198.1 (dd, $^2J_{CP}$ = 8 × 34 Hz, CO), 38.5 (s, 1*C*Me$_3$), 38.6 (s, 1*C*Me$_3$), 30.1 [s, 2C(*C*H$_3$)$_3$]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2099 cm^{-1} (w), 2025 (s, sh), 1730 (m). − MS (FAB); *m/z* (%): 921 [M^+ − CH_3] (27), 852 [M^+ − 3 CO] (100), 561 [M^+ − 2 CO − L] (51), 533 [M^+ − 3 CO − L] (76). − $C_{45}H_{44}F_6N_3O_4P_3F_6W$ (1081.63): calcd. C 49.97, H 4.10, N 3.88; found C 49.89, H 3.99, N 3.91.

***trans,trans*-HW(CO)$_2$(NO)(Ph$_2$-*tert*-Bupy)$_2$ (15):** To a solution of **14** (109 mg, 0.101 mmol) and **6** (120 mg, 0.379 mmol) in THF (3 mL) was added sodium tetrahydroborate (15 mg, 0.397 mmol). Upon addition of the tetrahydroborate, the reaction mixture slowly evolved carbon monoxide and darkened in colour from yellow to dark-orange. After stirring for 30 min at 40 °C, the mixture was concentrated to a volume of 0.5 mL in vacuo and ethanol (4 mL) was added to induce precipitation of the yellow product. After filtration and washing of the collected solid with ethanol (2 × 2 mL) and pentane (2 × 2 mL), a yellow powder was obtained. Yield: 25 mg (0.038 mmol, 38%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.70−7.25 (m, 26 H, Ph + py), 1.27 (s, 18 H, CH_3), −0.18 (t, 1 H, J_{PH} = 22.5 Hz, J_{WH} = 31.0 Hz). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 29.4 (s, J_{PW} = 287 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 217.0 (t, $^2J_{CP}$ = 7 Hz, CO), 38.2 (s, *C*Me$_3$), 30.1 [s, C(*C*H$_3$)$_3$]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1931 cm^{-1} (s), 1685 (m), 1594 (m). − MS (FAB); *m/z* (%): 797 [M^+] (4), 769 [M^+ − CO] (20), 740 [M^+ − 2CO] (25). − $C_{44}H_{45}N_3O_3P_2W$ (909.66): calcd. C 58.10, H 4.99, N 4.62; found C 58.27, H 5.13, N 4.39.

[W(CO)$_2$(NO)(Me$_2$Ppy)$_3$][BF$_4$] (16): To a solution of [W(CH_3CN)$_3$(CO)$_2$(NO)][BF_4] (960 mg, 1.88 mmol) in dichloromethane (15 mL) was added Me$_2$Ppy (790 mg, 5.68 mmol) and the reaction mixture was stirred for 1 h at room temperature. It was then concentrated to a volume of 5 mL in vacuo and carefully layered with diethyl ether. After 3 d at −30 °C, orange crystals had separated. Yield: 1.26 g (1.34 mmol, 90%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.73 (m, 3 H, py), 7.83 (m, 3 H, py), 7.51 (m, 3 H, py), 7.40 (m, 3 H, py), 1.89 (m, 12 H, CH_3), 1.79 (m, 6 H, CH_3). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −16.6 (d, $^2J_{PP}$ = 25 Hz, J_{PW} = 251 Hz), −21.9 (t, $^2J_{PP}$ = 25 Hz, J_{PW} = 165 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 208.2 (m, CO), 15.7 [m, P(CH_3)$_2$]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2029 cm^{-1} (s), 1955 (s), 1683 (m). − MS (FAB): *m/z* (%) = 687 [M^+] (82), 548 [M^+ − L] (70), 520 [M^+ − CO − L] (79), 492 [M^+ − 2 CO − L] (22). − $C_{23}H_{30}BF_4N_4O_3P_3WCH_2Cl_2$ (942.41): calcd. C 33.56, H 3.75, N 6.52; found C 33.78, H 3.57, N 6.92.

***cis/trans*-HW(CO)$_2$(NO)(Me$_2$Ppy)$_2$ (17):** To THF (6 mL) was added **16** (225 mg, 0.29 mmol) and sodium hydrotrimethoxyborate. The resulting mixture was stirred for 30 min at room temperature and then the solvent was removed in vacuo. The dark-red residue was extracted with pentane (3 × 5 mL) and the combined extracts were filtered through Celite. Evaporation of the solvent from the filtrate afforded an orange oil, which was taken up in dichloromethane (5 mL). To this solution, $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ (72 mg, 0.15 mmol) was added to trap uncoordinated Me_2Ppy. The reaction mixture was stirred for 30 min and then the solvent was evaporated in vacuo. The brown residue was extracted with pentane (3 × 5 mL) and the combined extracts were filtered through Celite and concentrated to dryness. The product was obtained as a mixture of isomers in the form of a yellow oil (*cis*/*trans* ratio, 20:80). Yield: 64 mg (0.117 mmol, 40%). − MS (FAB); *m*/*z* (%): 548 $[M^+]$ (66), 520 $[M^+ - CO]$ (100), 505 $[M^+ - 2\ CO - CH_3]$ (22), 492 $[M^+ - 2CO]$ (32), 477 $[M^+ - 2\ CO - CH_3]$ (16). − $C_{16}H_{21}N_3O_3P_2W$ (549.16): calcd. C 34.99, H 3.85, N 7.65; found C 35.03, H 3.96, N 7.58. − NMR data (*cis* isomer): ^1H NMR (300 MHz, C_6D_6): δ = 8.22 (m, 2 H, py), 7.60 (m, 2 H, py), 6.88 (m, 2 H, py), 6.42 (m, 2 H, py), 1.62 (m, 12 H, PCH_3), 0.22 (t, 1 H, J_{PH} = 27.2 Hz, J_{WH} = 33.3 Hz). − ^{31}P NMR (300 MHz, C_6D_6): δ = −15.1 (s, J_{PW} = 251 Hz). − ^{13}C NMR (500 MHz, C_6D_6): δ = 217.1 (m, CO), 19.0 [m, $P(CH_3)_2$]. − NMR data (*trans* isomer): ^1H NMR (300 MHz, C_6D_6): δ = 8.42 (m, 2 H, py), 7.85 (m, 2 H, py), 7.05 (m, 2 H, py), 6.49 (m, 2 H, py), 1.89 (m, 12 H, PCH_3), −0.81 (t, 1 H, J_{PH} = 25.6 Hz, J_{WH} = 30.2 Hz). − ^{31}P NMR (300 MHz, C_6D_6): δ = −11.1 (s, J_{PW} = 280 Hz). − ^{13}C NMR (500 MHz, C_6D_6): δ = 216.9 (t, $^2J_{CP}$ = 7 Hz, CO), 20.1 [m, $P(CH_3)_2$].

$[W(CO)_2(NO)(Me_2P$-*tert*-$Bupy)_3][BF_4]$ (18): To a solution of $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ (715 mg, 1.49 mmol) in dichloromethane (15 mL) was added an azeotropic mixture of Me_2P-*tert*-Bupy (1.31 g, ca. 4.5 mmol) and the reaction mixture was stirred for 18 h at room temperature. The resulting dark-orange solution was then concentrated to a volume of 2 mL, whereupon diethyl ether was added dropwise to induce precipitation of the orange product. After washing with diethyl ether (3 × 5 mL) and pentane (3 × 5 mL), the pure product was obtained as an orange solid. Yield: 1.26 g (1.34 mmol, 90%). − ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.74 (m, 3 H, py), 7.43 (m, 3 H, py), 7.25 (m, 1 H, py), 7.07 (m, 2 H, py), 1.90 (m, 12 H, CH_3), 1.72 (m, 6 H, CH_3), 1.37 (s, 18 H, *t*Bu), 1.36 (s, 9 H, *t*Bu). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −20.8 (d, $^2J_{PP}$ = 22.9 Hz, J_{PW} = 243 Hz), −21.9 (t, $^2J_{PP}$ = 23 Hz, J_{PW} = 158 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 208.3 (m, CO), 38.4 [s, C, $C(CH_3)_3$], 30.2 [s, C, $C(CH_3)_3$], 16.0 [m, $P(CH_3)_2$]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2026 cm^{-1} (s), 1957 (s), 1687 (m). − MS (FAB); *m*/*z* (%): 856 $[M^+]$ (80), 633 $[M^+ - CO - L]$ (12), 605 $[M^+ - 2\ CO - L]$ (60). − $C_{35}H_{54}BF_4N_4O_3P_3W$ (942.41): calcd. C 44.61, H 5.78, N 5.94; found C 44.33, H 5.55, N 5.72.

***cis*/*trans*-$HW(CO)_2(NO)(Me_2P$-*tert*-$Bupy)_2$ (19):** Compound **19** was prepared in the same manner as described for **17** by using **18** (62 mg, 0.066 mmol) as the starting complex; (*cis*/*trans* ratio 20:80) Yield: 30 mg (0.045 mmol, 69%). − MS (FAB); *m*/*z* (%): 645 $[M^+ - CH_3]$ (35), 632 $[M^+ - CO]$ (25), 587 $[M^+ - 2\ CO - CH_3]$ (22). − NMR data (*cis* isomer): ^1H NMR (300 MHz, CD_2Cl_2): δ = −0.35 (t, 1 H, J_{PH} = 27.2 Hz, J_{WH} = 33.3 Hz), other resonances partially obscured by those of the *trans* isomer. − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −15.3 (s, J_{PW} = 251 Hz). − NMR data (*trans* isomer): ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.7−7.2 (m, 4 H, py), 6.67 (m, 2 H, py), 2.00 (m, 12 H, PCH_3), 1.35 (s, 18 H, *t*Bu), −1.42 (t, 1 H, J_{PH} = 25.4 Hz, J_{WH} = 31.2 Hz). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −11.4 (s, J_{PW} = 279 Hz). − ^{13}C NMR (500 MHz, CD_2Cl_2): δ = 216.6 (t, $^2J_{CP}$ = 7 Hz, CO), 38.2 (s, CMe_3), 30.1 [s, $C(CH_3)_3$], 15.3 [m, $P(CH_3)_2$].

***cis*,*cis*-$[W(CO)(NO)(\eta^2\text{-}Ph_2Ppy)_2][BF_4]$ (20):** A suspension of **9a** (100 mg, 0.11 mmol) in toluene (10 mL) was stirred at 100 °C while the solvent was pumped off in a vacuum line to about half of the original volume over a period of 20 min. A further 5 mL of toluene was then added and the procedure was repeated. After cooling to room temperature, the solvent was decanted from the dark-orange residue and the latter was washed with THF (3 × 5 mL) and pentane (5 mL). The product could be recrystallized from CH_2Cl_2/Et_2O to give orange crystals. Yield: 68 mg (0.079 mmol, 71%). − ^1H NMR (300 MHz, CD_3NO_2): δ = 9.30 (m, 1 H), 8.36 (m, 1 H), 7.95 (m, 6 H), 7.74 (m, 4 H), 7.56 (m, 9 H), 7.30 (m, 3 H), 7.05 (m, 2 H), 6.48 (m, 2 H). − ^{31}P NMR (300 MHz, CD_3NO_2): δ = 2.3 (d, J_{PP} = 16 Hz, J_{PW} = 328 Hz), −12.8 (d, J_{PP} = 16 Hz, J_{PW} = 180 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 232.5 (d, $^2J_{CP}$ = 47 Hz, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1920 cm^{-1} (s), 1611 (s). − MS (FAB); *m*/*z* (%): 768 $[M^+]$ (34), 740 $[M^+ - CO]$ (5). − $C_{35}H_{28}BF_4N_3O_2P_2W$ (855.23): calcd. C 49.15, H 3.30, N 4.91; found C 49.32, H 3.20, N 4.83.

***trans*,*trans*-$[W(CO)(NO)(\eta^2\text{-}Ph_2Ppy)_2][BPh_4]$ (21):** To a solution of **9b** (60 mg, 0.05 mmol) in acetonitrile (1 mL) was added toluene (8 mL) and the mixture was slowly concentrated to a volume of 6 mL in vacuo at a bath temperature of 80 °C. The concentrated solution was then stirred for 2 h at 95 °C under slightly reduced pressure. After pumping off the solvent, the red residue was redissolved in acetonitrile (1 mL) and toluene (8 mL). After stirring for a further 3 h at 95 °C, the volume was reduced to 2 mL in vacuo. The mixture was filtered and a red solid was crystallized at −30 °C by layering a cold dichloromethane solution with diethyl ether and leaving the system to stand overnight. Yield: 35 mg (0.029 mmol, 59%). − ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.2−6.7 (m, Ph + py). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −0.5 (m, 2 P, AB system, J_{PaPb} = 121 Hz, J_{PaW} = 277 Hz, J_{PbW} = 299 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 237.1 (m, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1920 cm^{-1} (s), 1625 (s). − MS (FAB); *m*/*z* (%): 768 $[M^+]$ (18). − $C_{59}H_{48}BN_3O_2P_2W \cdot CH_2Cl_2$ (1172.6): calcd. C 61.46, H 4.30, N 3.58; found C 61.86, H 4.44, N 3.88.

***cis*,*cis*-$[W(CO)_2(NO)(Me_2Ppy)(\eta^2\text{-}Me_2Ppy)][BF_4]$ (22):** To a solution of $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ (214 mg, 0.447 mmol) in THF (12 mL) was added Me_2Ppy (125 mg, 0.9 mmol). The transient formation of a yellow suspension could be observed before the reaction mixture became homogeneous again. After stirring overnight at room temperature, half of the solvent was evaporated in vacuo. Toluene (6 mL) was then added, stirring was continued for a further 5 min, and then the solvent was removed in vacuo. The resulting dark-yellow oil was taken up in dichloromethane (5 mL) and the product was precipitated by the slow addition of pentane. The supernatant was decanted off and the residue was washed several times with pentane to afford a yellow oil. Yield: 197 mg (0.31 mmol, 69%). − ^1H NMR (300 MHz, −15 °C, $C_2Cl_4D_2$): δ = 7.49 (m, 1 H, py), 7.29 (m, 1 H, py), 7.14 (m, 1 H, py), 7.00 (m, 2 H, py), 6.76 (m, 1 H, py), 6.67 (m, 1 H, py), 6.49 (m, 1 H, py), 1.53 (m, 6 H, PCH_3), 1.33 (m, 12 H, PCH_3). − ^{31}P NMR (300 MHz, −15 °C, $C_2Cl_4D_2$): δ = −9.8 (d, $^2J_{PP}$ = 25 Hz, J_{PW} = 256 Hz), −48.2 (d, $^2J_{PP}$ = 25 Hz, J_{PW} = 220 Hz). − ^{13}C NMR (300 MHz, −15 °C, $C_2D_2Cl_4$): δ = 213.0 (dd, $^2J_{CP}$ = 5 × 3 Hz, CO), 208.2 (dd, $^2J_{CP}$ = 5 × 41 Hz, CO), 15.2 [m, $P(CH_3)_2$], 11.39 [m, $P(CH_3)_2$]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2035 cm^{-1} (s), 1962 (s), 1635 (m). − MS (FAB); *m*/*z* (%): 548 $[M^+]$ (50), 520 $[M^+ - CO]$ (22), 492 $[M^+ - 2CO]$ (6).

$[W(CO)_2(CH_3CN)(NO)(Me_2P$-*tert*-$Bupy)_2][BF_4]$ (23a): To a solution of $[W(CH_3CN)_3(CO)_2(NO)][BF_4]$ (115 mg, 0.24 mmol) in THF (5 mL) was added Me_2P-*tert*-Bupy (125 mg, 0.9 mmol). After stirring the reaction mixture for 3 h at 60 °C, hexane was added to precipitate a yellow oil. The supernatant solution was decanted off and the residue was taken up in acetonitrile (2 mL). This solution was stirred for 5 min and then the solvent was removed under high vacuum. The residual yellow oil was taken up in dichloromethane (2 mL) and precipitated once more by the slow addition of hexane. The residue was finally taken up in toluene (5 mL), filtered through Celite, and dried under high vacuum. Yield: 145 mg (0.185 mmol, 77%). − ^{1}H NMR (300 MHz, [D$_8$]toluene): δ = 7.52 (m, 4 H, py), 6.96 (m, 2 H, py), 2.26 (s, 3 H, CH_3CN), 1.70 (m, 12 H, PMe_2), 1.26 (s, 18 H, *t*Bu). − ^{31}P NMR (300 MHz, [D$_8$]toluene): δ = −12.8 (s, J_{PW} = 254 Hz). − ^{13}C NMR (300 MHz, [D$_8$]toluene): δ = 208.9 (m, CO), 38.0 (s, *C*Me$_3$), 30.1 [s, C(*C*H$_3$)$_3$], 13.4 [m, P(CH$_3$)$_2$], 2.8 (s, *C*H$_3$CN). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2308 cm^{-1} (w), 2040 (s), 1967 (s), 1682 (m). − MS (FAB); *m*/*z* (%): 701 [M$^+$] (20), 660 [M$^+$ − CH$_3$CN] (18), 632 [M$^+$ − CO − CH$_3$CN] (28), 604 [M$^+$ − 2 CO − CH$_3$CN] (87), 544 [M$^+$ − 2 CO − CH$_3$CN − NO − 2 CH$_3$] (16). − An unidentified phosphane impurity amounting to 5% could not be removed; no elemental analysis was attempted (see text).

[W(CO)$_2$(CH$_3$CN)(NO)(Me$_2$P-*tert*-Bupy)$_2$][TFPB] (23b): A mixture of **23a** (276 mg, 0.35 mmol) and Na[TFPB] (336 mg, 0.38 mmol) was stirred for 45 min at room temperature. After evaporation of the solvent in vacuo, the residue was extracted with dichloromethane and the combined extracts were filtered through Celite. Removal of the solvent from the filtrate left the product as a yellow oil. Yield: 460 mg (0.294 mmol, 77%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.74 (br., 8 H, Ph), 7.58 (br., 4 H, Ph), 7.43 (m, 4 H, py), 7.23 (m, 2 H, py), 2.20 (s, 3 H, CH_3CN), 1.80 (m, 12 H, PMe_2), 1.35 (s, 18 H, *t*Bu). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = −13.6 (s, J_{PW} = 254 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 207.9 (m, CO), 171.1 (d, $^3J_{CP}$ = 7 Hz, *ipso*-C, py), 162.3 (q, *ipso*-C, BPh$_4$), 158.1 (d, $^1J_{CP}$ = 34 Hz, *ipso*-C, py), 38.0 (s, *C*Me$_3$), 30.1 [s, C(*C*H$_3$)$_3$], 14.2 [m, P(CH$_3$)$_2$], 4.0 (s, *C*H$_3$CN). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2308 cm^{-1} (w), 2040 (s), 1967 (s), 1682 (m). − MS (FAB); *m*/*z* (%): 701 [M$^+$] (20), 660 [M$^+$ − CH$_3$CN] (18), 632 [M$^+$ − CO − CH$_3$CN] (28), 604 [M$^+$ − 2 CO − CH$_3$CN] (87), 544 [M$^+$ − 2 CO − CH$_3$CN − NO − 2 CH$_3$] (16). − $C_{58}H_{51}BF_{24}N_4O_3P_2W$ (1564.3): calcd. C 44.93, H 3.32, N 3.58; found C 44.42, H 3.31, N 2.94.

***trans*-W(CO)(NO)(Ph$_2$Ppy)$_2$(η^2-CH$_3$CO$_2$) (24):** To a solution of **10** (30 mg, 0.038 mmol) in a mixture of dichloromethane (0.5 mL) and 2-propanol (2 mL), acetic acid (0.2 mL) was added at −30 °C. The resulting mixture was allowed to warm to room temperature, whereupon slow gas evolution was observed. After stirring for 30 min, the mixture was concentrated to a volume of 1 mL and the product was precipitated by slowly adding pentane. After subsequent washing with pentane, a red powder was obtained. Yield: 21 mg (0.025 mmol, 64%). − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.71 (m, 2 H, py), 7.60−7.20 (m, 26 H, Ph), 0.54 (s, 3 H, CH$_3$). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 39.3 (s, J_{PW} = 308 Hz). − ^{13}C NMR (500 MHz, CD_2Cl_2): Decomposition was observed when the sample was left overnight. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1894 cm^{-1} (s), 1578 (m). − MS (FAB); *m*/*z* (%): 827 [M$^+$] (2), 799 [M$^+$ − CO] (3), 768 [M$^+$ − CO(O)CH$_3$] (18). − $C_{37}H_{31}N_3O_4P_2W$ (827.47): calcd. C 53.71, H 3.78, N 5.08; found C 52.67, H 3.56, N 5.18.

***trans*-IW(CO)$_2$(NO)(Ph$_2$Ppy)$_2$ (25):** To a solution of **10** (24 mg, 0.03 mmol) in dichloromethane (0.7 mL), hydroiodic acid (0.05 mL, 0.75 M in chloroform) was added at room temperature. The colour of the solution changed from yellow to orange and gas evolution was observed. After 10 min, the solvent was removed under reduced pressure and the orange product was washed several times with pentane. Yield: 19 mg (0.021 mmol, 69%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.83 (m, 2 H, py), 7.7−7.2 (m, 26 H, Ph). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 13.0 (s, J_{PW} = 289 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 205.6 (t, $^2J_{CP}$ = 6 Hz, CO). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2008 cm^{-1} (w), 1961 (s), 1638 (m). − MS (FAB); *m*/*z* (%): 867 [M$^+$ − 2 CO] (11), 796 [M$^+$ − I] (22), 768 [M$^+$ − I − CO] (46). − $C_{36}H_{28}IN_3O_3P_2W$ (923.34): calcd. C 46.83, H 3.06, N 4.55; found C 46.42, H 3.13, N 4.52.

***trans*-W(HCO$_2$)(CO)$_2$(NO)(Ph$_2$Ppy)$_2$ (26):** Carbon dioxide was slowly bubbled through a solution of **9** (50 mg, 0.063 mmol) in THF (4 mL) at room temperature. The colour of the solution slowly changed from yellow to orange. After 30 min, it was concentrated to a volume of 1 mL and the product was precipitated by adding diethyl ether. After washing with pentane, an orange powder was obtained. Yield: 32 mg (0.039 mmol, 60%). − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.80 (m, 2 H, py), 7.66−7.28 (m, 26 H, Ph), 7.06 [s, 1 H, OC(O)H]. − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 28.2 (s, $^2J_{PW}$ = 299 Hz). − ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 210.4 (t, $^2J_{CP}$ = 5 Hz, CO), 166.39 [s, OC(O)H]. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2050 cm^{-1} (w), 1962 (s), 1622 (br.). − MS (FAB); *m*/*z* (%): 796 [M$^+$ − OC(O)H] (18), [M$^+$ − 2 CO] (45), 768 [M$^+$ − CO − OC(O)H] (70), [M$^+$ − 2 CO − OC(O)H] (28).

***trans*-W{η^2-(*Z*)-C(CO$_2$Me)=CH[C(O)OMe]}(CO)(NO)(Ph$_2$Ppic)$_2$ (27):** To a solution of **12** (12 mg, 14.5 µmol) in [D$_8$]THF (0.7 mL) was added dimethyl acetylenedicarboxylate (2 µL, 15.5 µmol) and the reaction was monitored by ^{1}H-NMR spectroscopy. After 5 min at room temperature, the reaction was complete and a dark-red solution had been obtained. The solvent was evaporated in vacuo and the residual solid was washed several times with diethyl ether and pentane. Yield: 10 mg (10.6 µmol, 73%). − ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 7.70 (m, 8 H, Ph), 7.47 (m, 2 H, py), 7.28 (m, 12 H, Ph), 7.22 (m, 2 H, py), 7.00 (m, 2 H, py), 6.89 (t, 1 H, $^4J_{PH}$ = 3.4 Hz, vinyl H), 2.92 (s, 3 H, OCH$_3$), 2.86 (s, 3 H, OCH$_3$), 2.41 (s, 6 H, pic-CH$_3$). − ^{31}P NMR (300 MHz, [D$_8$]THF): δ = 31.7 (s, J_{PW} = 295 Hz). − ^{13}C NMR (300 MHz, [D$_8$]THF): δ = 245.8 (t, $^2J_{CP}$ = 5 Hz, CO), 222.4 (t, $^2J_{CP}$ = 10 Hz, α-vinyl C), 183.2 (s, *C*OOMe), 179.3 (s, *C*OOMe), 160.7 (t, $^1J_{CP}$ = 30 Hz, *ipso*-C, py), 53.8 (s, OCH$_3$), 50.9 (s, OCH$_3$), 24.5 (s, CH$_3$); the vinylic carbon signal is obscured by aromatic resonances. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1935 cm^{-1} (s), 1689 (m), 1595 (m). − MS (FAB); *m*/*z* (%): 938 [M$^+$] (2), 910 [M$^+$ − CO] (5), 798 [M$^+$ − MeO$_2$CC=CCO$_2$Me] (25).

***trans,trans*-WD(CO)$_2$(NO)(Ph$_2$Ppy)$_2$ (28):** To a solution of **10** (40 mg, 0.050 mmol) in dichloromethane, [D$_1$]methanol (0.5 mL) was added at 0 °C. After stirring for 1 h at exactly 0 °C, the deuterated product was precipitated from the reaction mixture by adding further [D$_1$]methanol (3 mL). The solvents were decanted and the yellow solid was dried in vacuo. Yield: 35 mg (44 µmol, 88%). − ^{2}H NMR (300 MHz, CH_2Cl_2): δ = −0.32 (br. s). − ^{31}P NMR (300 MHz, CD_2Cl_2): δ = 31.0 (t, $^2J_{PD}$ = 3 Hz). − IR (CH_2Cl_2): $\tilde{\nu}$ = 1921 cm^{-1} (s), 1628 (m); W−D not observed. − $C_{36}H_{28}DN_3O_3P_2W$ (798.45): calcd. C 54.15, H 3.53, N 5.26; found C 53.85, H 3.86, N 5.27.

X-ray Structural Determinations: Data collection for all structures was performed in a cold N$_2$ stream (see Table 1) with a Nicolet−Siemens P4 diffractometer in the range 2.0° ≤ φ ≤ 25.0°. The structures of complexes **9**, **11**, and **20** were solved by Patterson synthesis (SHELXS-86)[25] and refined using SHELXTL-PLUS[26] for **11** and **20** or SHELXL-93[27] for **9**. The structure of complex **14** was solved by direct methods (SIR-92,[28] SHELXTL-PLUS). Pertinent crystallographic parameters for the four structures are listed in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cam-

Table 1. Experimental conditions and crystallographic data for **9a**, **11**, **14**, and **20**

	9a	**11**	**14**	**20**
Empirical formula	$C_{36}H_{28}BF_4N_3O_3P_2W$	$C_{38}H_{32}BF_4N_3O_3P_2WCH_2Cl_2$	$C_{45}H_{44}F_6N_3O_4P_3W$	$C_{37}H_{32}BCl_4F_4N_3O_2P_2WCH_2Cl_2$
Molecular mass	883.21	996.23	1081.62	1025.7
Colour	yellow	yellow	yellow	red
Cryst. size [mm]	0.2 × 0.3 × 0.3	0.25 × 0.35 × 0.40	0.15 × 0.20 × 0.35	0.25 × 0.35 × 0.35
Cryst. system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	17.051(6)	12.160(3)	18.059(3)	12.870(3)
b [Å]	11.344(2)	10.521(4)	11.760(3)	12.938(2)
c [Å]	18.515(3)	34.088(8)	21.895(5)	13.161(3)
β [°]	107.06	96.23(2)	96.52(2)	85.98(2)
V [Å^3]	3423.7(15)	4335(2)	4691.9	2026.3(6)
Z	4	4	4	2
$D_{\text{calcd.}}$ [g/cm^3]	1.713	1.66	1.56	1.68
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
T [K]	203	178	173	183
No. of rflns. collected	7489	7615	7862	7110
No. of unique rflns.	5105	8503	5528	6899
$wR2$	0.101	0.600	0.520	0.360
$R1$	5.22	4.1	5.0	2.8
goodness-of-fit	1.192	1.153	1.037	1.147

bridge Crystallographic Data Centre as supplementary publication nos. CCDC-136277−136280. Copies of the data can be obtain free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336003; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: The calculations utilized the Amsterdam Density Functional package ADF release 2.0.1 and release 2.3. The ADF basis set III was chosen for the main group elements, whereas W was described with a modified basis set IV with 6p functions. The self-consistent DFT calculations were based on the local exchange correlation potential of Vosko, Wilk, and Nussair,[29] with the addition of gradient corrections due to Becke[30] and Perdew[31] (NL-SCF). Relativistic effects were included using a quasi-relativistic approach.[32] The accuracy parameter for the numerical integration was set to 4.0. All molecules were fully optimized at the quantum mechanical level. Default convergence criteria[33] were employed, except for the gradients in the geometry optimizations, which were set to 0.006 hartree/Å or hartree/radian, respectively. In the transition state search, the W−N(pyridyl) distances were assumed to be equal.

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