Intramolecular Hydrogen-Bonding, Cation−π, and π-Stacking Interactions Affecting *cis*/*trans* Isomerization: Hexacarbonyltungsten Derivatives of Pyridyl-Substituted Arylphosphane Ligands

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Keywords: *cis*/*trans* Isomerism / Hydrogen bonding / Intramolecular interactions / Phosphanes / Tungsten

A series of triphenylphosphane- and diphenyl(2-pyridyl)phosphane-substituted tetracarbonyltungsten derivatives has been prepared. Attractive intramolecular interactions between the phosphane ligands have been studied in both the neutral and protonated complexes; π-stacking, hydrogen-bonding, and cation–π bonding interactions were identified and were found to have an influence on the *cis*/*trans* isomerism of the complexes. It was found that the *cis*/*trans* isomerism could be switched by protonation or deprotonation of the diphenyl(2-pyridyl)phosphane derivatives. The complexes have been characterized by ^{31}P-, ^{1}H-, and ^{13}C NMR spectroscopy, X-ray crystallography, IR spectroscopy, and mass spectrometry.

Introduction

Supramolecular complexation through hydrogen-bonding, cation−π, or π-stacking interactions is an expanding area of research in chemistry, and is of enormous potential with regard to applications in several fields of chemistry and biology.[1] For example, enzyme catalysis is typically effected by attractive interactions between the enzyme and the substrate.

In organometallic chemistry, repulsive interactions between ligands are important parameters in determining the structures and reactivities of complexes. Supramolecular attractive interactions between ligands in the coordination sphere of a single transition metal complex have not attracted such attention. There are, however, examples of intramolecular π-stacking in transition metal complexes, both interligand[2,3] and intraligand.[4−6] There have also been studies concerning interligand hydrogen bonding in biochemically interesting purine and pyrimidine complexes,[7,8] theoretical studies of interligand hydrogen bonding between nitrogen donor ligands and small ligands such as H_2O, HF, or NH_3,[9,10] and some studies concerning interligand CH−π interactions.[11,12]

The full potential of attractive interactions between the ligands of organometallic complexes has not been evaluated: Attractive interactions between the ligands or between a ligand and a substrate offer a very promising approach to organometallic catalysis. In metalloenzymes, for instance, the interactions at the active site of an enzyme−substrate complex have been regarded as ligand−ligand interactions around the metal atom, playing a vital role in enzyme catalysis.[11]

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In this work, attractive supramolecular interactions between phosphane ligands are used to modify *cis*/*trans* isomerization in complexes of the type $[W(CO)_4LL']$. Complexes $[W(CO)_4(PPh_3)_2]$ (**1**),[13] $[W(CO)_4(py)(PPh_3)]$ (**2**), $[W(CO)_4\{P(2\text{-py})Ph_2\}_2]$ (**3**), $[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}\{P(2\text{-py})Ph_2\}](ClO_4^-)$ (**4**), $[W(CO)_4\{P(2\text{-py})Ph_2\}(PPh_3)]$ (**5**), and $[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}(PPh_3)](ClO_4^-)$ (**6**)[13] have been used in this study.

Results

Synthesis of the Complexes

The aim of this study was to prepare and evaluate complexes in which phosphane ligands would be able to exhibit intramolecular attractions. These interactions could be π-stacking in neutral complexes, or cation−π or hydrogen-bonding interactions in cationic complexes. Sterically similar diphenyl(2-pyridyl)phosphane $[P(2\text{-py})Ph_2]$ and triphenylphosphane (PPh_3) were chosen as ligands.

Complexes $[W(CO)_4(PPh_3)_2]$ (**1**), $[W(CO)_4(py)(PPh_3)]$ (**2**), and $[W(CO)_4\{P(2\text{-py})Ph_2\}_2]$ (**3**) were synthesized by treating $[W(CO)_4(py)_2]$ with the appropriate phosphane ligand in benzene solution at 40−45 °C overnight.[14] When the reaction was performed using PPh_3 as the ligand, a mixture of complexes **1** and **2** was obtained. When $P(2\text{-py})Ph_2$ was used as the ligand, the only isolable product from the reaction was **3**, with no trace of a derivative analogous to **2**. The complex $[W(CO)_4\{P(2\text{-py})Ph_2\}(PPh_3)]$ (**5**) was prepared from **2** by the method described above. In the case of complexes **1**, **3**, and **5**, a mixture of *cis* and *trans* isomers was produced. When these complexes were purified by column chromatography, the *cis* isomer was eluted slightly faster than the *trans* isomer, but the bands could not be completely resolved. Complexes **3** and **5** were protonated with perchloric acid in chloroform solution to give the com-

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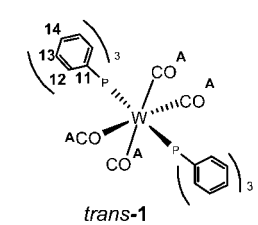
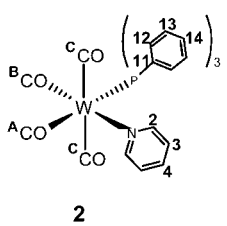
pounds $[W(CO)_4\{P(2\text{-}pyH)^+Ph_2\}\{P(2\text{-}py)Ph_2\}](ClO_4^-)$ (**4**) and $[W(CO)_4\{P(2\text{-}pyH)^+Ph_2\}(PPh_3)](ClO_4^-)$ (**6**).

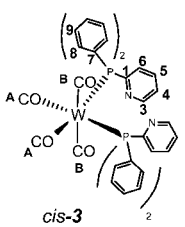
Solution Behavior of the Complexes

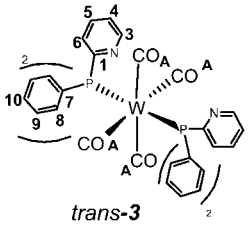
All the reported complexes were characterized by NMR spectroscopy. ^1H NMR spectroscopic data are reported in the Exp. Sect. $^{13}C\{^1H\}$ NMR data for complexes **1**−**6** are presented in Table 1. In the case of complexes forming a mixture of *cis* and *trans* isomers, where possible, the spectra of the individual isomers were measured starting from the pure isomer obtained by column chromatography. In the case of ^{13}C NMR spectroscopy, however, the time required for spectral acquisition was too long to keep the isomer

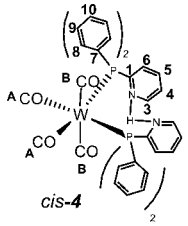
Table 1. $^{13}C\{^1H\}$ NMR spectra of compounds **1**−**6**

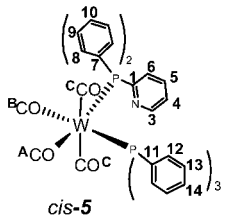


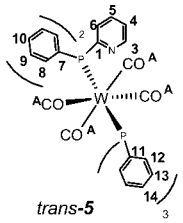


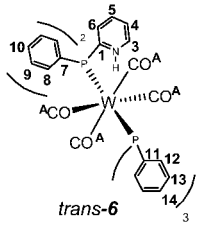












	trans-**1**[a]	*cis*-**2**	*cis*-**3**[a]	*trans*-**3**[a]	*cis*-**4**	*cis*-**5**	*trans*-**5**	*trans*-**6**
C^A (ppm)	203.68	208.69	203.03	202.95	202.03	intensity	202.95	201.78
$^2J_{CP}$ (Hz)	6.4 (t)	36.5 (d)	7.0 (t)	6.3 (t)	6.8 (t)	too low	6.3 (dd)	6.3 (dd)
C^B (ppm)	−	210.00	205.43	−	203.11	intensity	−	−
$^2J_{CP}$ (Hz)		4.9 (d)	(m)		9.9(t)	too low		
C^C (ppm)	−	204.72	−	−	−	−	−	−
$^2J_{CP}$ (Hz)		6.8 (d)						
C^1 (ppm)	−	−	161.82	162.98	156.29	158−172	158−172	157.85
$^1J_{CP}$ (Hz)			(m)	(m)	48 (d)			9.2 (d)
C^2 (ppm)	−	155.41	−	−	−	−	−	−
$^3J_{CP}$ (Hz)		1.7 (d)						
C^3 (ppm)	−	124.66	149.31	149.40	147.52	149.31	149.38	145.18
$^3J_{CP}$ (Hz)		(s)	(m)	7.3 (dd)	4.2 (dd)	16.1 (d)	15.8 (d)	6.4 (d)
C^4 (ppm)	−	135.72	122.7	122.78	126.07	122.99	122.87	126.46
$^4J_{CP}$ (Hz)		(s)	(s)	(s)	(s)	(s)	(s)	(s)
C^5 (ppm)	−	−	135.32	135.46	141.02	135.33	135.77	143.96
$^3J_{CP}$ (Hz)			(m)	3.6 (dd)	(s)	5.9 (d)	12.5 (d)	(s)
C^6 (ppm)	−	−	127.26	127.24	127.80	127.01	127.27	128.61
$^2J_{CP}$ (Hz)			(m)	11.3 (dd)	4.2 (dd)	18.0 (d)	22.0 (d)	5.7 (d)
C^7 (ppm)	−	−	135.93	137.61	134.78	137.47	137.47	134.13
$^1J_{CP}$ (Hz)			(m)	20.7 (dd)	22.0 (d)	(d)	41.1(d)	13.4 (d)
C^8 (ppm)	−	−	133.94	135.53	133.57	133.84	133.52	133.35
$^2J_{CP}$ (Hz)			5.7 (dd)	5.7 (dd)	6.3 (dd)	11.3 (d)	11.5 (d)	13.2 (d)
C^9 (ppm)	−	−	127.98	128.02	129.48	127.92	128.07	128.44
$^3J_{CP}$ (Hz)			(m)	4.8 (dd)	4.7 (dd)	9.5 (d)	9.5 (d)	9.7 (d)
C^{10} (ppm)	−	−	129.52	129.41	131.47	129.65	129.49	131.4−130.2
$^4J_{CP}$ (Hz)			(s)	(s)	(s)	2.2 (d)	1.5 (d)	
C^{11} (ppm)	137.87	134.33	−	−	−	138.00	138.00	136.44
$^1J_{CP}$ (Hz)	20.2 (dd)	36.7 (d)				(d)	40.3 (d)	43.1 (d)
C^{12} (ppm)	133.09	133.35	−	−	−	133.52	133.09	132.99
$^2J_{CP}$ (Hz)	5.9 (dd)	11.8 (d)				11.5 (d)	11.6 (d)	11.5 (d)
C^{13} (ppm)	128.07	128.32	−	−	−	127.92	128.05	128.07
$^3J_{CP}$ (Hz)	4.7 (dd)	9.2 (d)				9.5 (d)	9.5 (d)	9.5 (d)
C^{14} (ppm)	129.34	129.61	−	−	−	129.38	129.32	129.7−130.3
$^4J_{CP}$ (Hz)	(s)	1.7 (d)				1.5 (d)	1.5 (d)	

[a] Signals labeled dd appeared as triplets in the spectra.

pure during the measurements. In the case of complex **5** (Table 1), initial measurements were made on the mixture of *cis* and *trans* isomers as these could not be separated. The data obtained for the isomeric mixture were interpreted with the help of 2D HSQC spectra.

In the $^{13}C\{^1H\}$ NMR spectra of the symmetrically substituted complexes *trans*-**1**, *cis*-**3**, *trans*-**3**, and *cis*-**4**, the phosphane ligands are seen to be coupled,[15] causing the ^{13}C-^{31}P coupled resonance peaks to appear as pseudo triplets in the spectra (denoted as doublets of doublets in Table 1). In the case of unsymmetrical complexes, the spectra show normal doublets due to ^{13}C-^{31}P coupling.

$^{31}P\{^1H\}$NMR spectroscopic data for complexes **1** and **3**−**6** are presented in Table 2. The table also shows the relative amounts of the *cis* and *trans* isomers of the complexes. These equilibrium percentages were checked after the solutions had been left to stand for a week. It has been shown in previous studies that increased steric bulk of the phosphane favors the *trans* isomers, arylphosphanes showing only a very small proportion of the *cis* isomer.[14]

Table 2. ^{31}P NMR chemical shifts and proportion of *cis* isomers for complexes **1**, **3**−**6**

	$^{31}P_{cis}$ ($^1J_{WP}$/Hz)		$^{31}P_{trans}$ ($^1J_{wp}$/Hz)		% *cis*
	PPh_3	$PPyPh_2$	PPh_3	$PPyPh_2$	
1	23 (229)	−	28 (238)	−	32
3	−	26 (236)	−	30 (285)	56
4	−	28 (244)	−	34 (288)[d][d][e]	100
5	24[a]	25[a]	29 (269)[b]	30 (270)[b]	41
6	21[c]	34[c]	24 (275)[d]	38 (297)[d]	14

[a] d, $^2J_{pp}$ = 24 Hz, $^1J_{WP}$ not shown. − [b] d, $^2J_{pp}$ = 58 Hz. − [c] d, $^2J_{pp}$ = 23 Hz, $^1J_{WP}$ not shown. − [d] d, $^2J_{pp}$ = 61 Hz. − [e] Measured immediately after protonation, before disappearance of the signal.

In this study, complex $[W(CO)_4(PPh_3)_2]$ (**1**) behaved as expected, giving 32% of the *cis* isomer in $CDCl_3$ solution. On replacing one or two of the PPh_3 ligands by P(2-py)Ph_2, the amount of the *cis* isomer increased, even though the steric properties of the ligands were essentially unchanged. Thus, when one of the PPh_3 ligands was replaced by P(2-py)Ph_2 (complex **5**), the *cis* content increased to 41%, and when both of the PPh_3 ligands were replaced by P(2-py)Ph_2 (complex **3**), the *cis* content increased further to 56%. When complex **3** was protonated to give $[W(CO)_4\{P(2\text{-}pyH)^+Ph_2\}\{P(2\text{-}py)Ph_2\}](ClO_4^-)$ (**4**), the equilibrium changed entirely in favor of the *cis* form within a few hours. On protonation of complex **5** to give $[W(CO)_4\{P(2\text{-}pyH)^+Ph_2\}(PPh_3)](ClO_4^-)$ (**6**), the opposite occurred, and the equilibrium was shifted almost totally in favor of the *trans* form. These protonation reactions proved to be reversible: By adding base to a solution of **4** or **6**, the original *cis*/*trans* ratio was re-established within a few hours in the case of complex **4** or after standing overnight in the case of complex **6**.

X-ray Crystallography

Crystal structures were determined for complexes **2** and **3**. The structures of complexes **1** and **4** have been published in a preliminary communication.[13] Complex **5** did not crystallize adequately, while complex **6** decomposed upon attempted crystallization. Selected bond lengths and angles in all the structures are presented in Table 3 and Table 4. The determined crystal structures correspond to the major isomers in solution.

All the complexes were found to have a slightly distorted octahedral geometry, the angle between the ligands being widened in the *cis*-disubstituted derivatives: The angles between the phosphane ligands in diphosphane derivatives **3** and **4** were found to be 99.7 and 95.7°, respectively, while in the sterically less crowded triphenyl(2-pyridiyl)phosphane derivative **2** (Figure 1), the N−W−P angle was found to be 91.6°. Bond lengths around the metal centers reflect the relative *trans* effects of N, P and CO donors.

Complex $[W(CO)_4(PPh_3)_2]$ (**1**) crystallized in the *trans* form, as expected for a bulky phosphane ligand.[14] Complex $[W(CO)_4(py)(PPh_3)]$ (**2**, Figure 1) crystallized in the *cis* form, as found in solution. In the latter case, there is little

Table 3. Bond lengths [Å] around the metal centers in complexes **1**−**4**

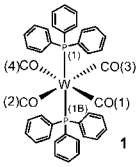
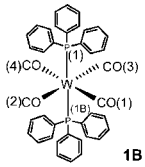
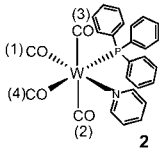
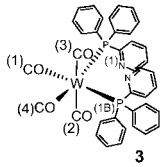
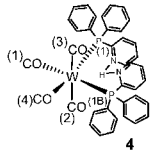
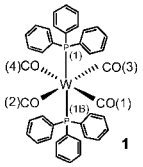
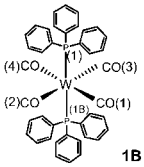
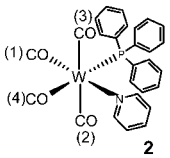
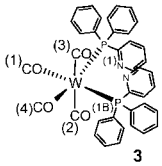
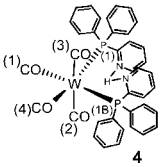
	 1	 1B	 2	 3	 4
W–P(1)	2.4789(8)	2.4889(8)	2.5396(9)	2.5562(4)	2.5170(7)
W–P(1B)	2.4789(8)	2.4689(8)	–	2.5562(4)	2.5482(7)
W–N(1)	–	–	2.287(3)	–	–
W–C(1)	2.045(4)	2.028(3)	1.962(4)	1.9703(18)	2.000(3)
W–C(2)	2.036(2)	2.034(3)	2.026(4)	2.040(2)	2.038(3)
W–C(3)	2.036(2)	2.031(3)	2.013(4)	2.040(2)	2.041(3)
W–C(4)	2.045(4)	2.058(3)	1.994(4)	1.9703(18)	1.991(3)
C(1)–O(1)	1.141(4)	1.141(4)	1.169(5)	1.163(2)	1.142(4)
C(2)–O(2)	1.146(4)	1.137(4)	1.155(5)	1.141(2)	1.143(4)
C(3)–O(3)	1.146(4)	1.148(4)	1.154(5)	1.141(2)	1.139(4)
C(4)–O(4)	1.141(4)	1.128(4)	1.147(5)	1.163(2)	1.147(4)

Table 4. Bond angles [°] around the metal centers in complexes **1**–**4**

	 1	 1B	 2	 3	 4
P(1)–W–C(1)	88.03(10)	95.16(10)	88.73(12)	90.62(5)	87.51(8)
P(1)–W–C(2)	90.66(9)	89.12(9)	90.33(11)	85.20(5)	96.90(8)
P(1)–W–C(3)	89.34(9)	90.71(9)	91.41(12)	94.96(5)	89.92(8)
P(1)–W–C(4)	91.97(10)	87.95(9)	176.85(11)	166.97(5)	170.88(9)
P(1)–W–N(1)	–	–	91.55(8)	–	–
P(1B)–W–P(1)	180.0	176.32(2)	–	99.70(2)	95.72(2)
P(1B)–W–C(1)	91.97(10)	88.32(10)	–	166.97(5)	175.44(9)
P(1B)–W–C(2)	89.34(9)	89.55(9)	–	94.96(5)	85.39(8)
P(1B)–W–C(3)	90.66(9)	90.79(9)	–	85.20(5)	93.85(7)
P(1B)–W–C(4)	88.03(10)	88.63(9)	–	90.62(5)	92.96(9)
N(1)–W–C(1)	–	–	177.83(13)	–	–
N(1)–W–C(2)	–	–	91.33(13)	–	–
N(1)–W–C(3)	–	–	90.18(15)	–	–
N(1)–W–C(4)	–	–	91.33(13)	–	–
C(1)–W–C(2)	90.45(12)	92.34(12)	90.82(15)	93.81(7)	91.04–(11)
C(1)–W–C(3)	89.55(12)	84.95(12)	87.66(17)	86.00(7)	89.36(11)
C(1)–W–C(4)	180.0(2)	175.64(13)	88.34(15)	80.40(10)	83.98(12)
C(2)–W–C(3)	180.0	177.26(12)	177.66(17)	179.75(10)	173.18(11)
C(2)–W–C(4)	89.55(12)	90.75(12)	90.89(15)	86.00(7)	86.57(12)
C(3)–W–C(4)	90.45(12)	91.97(12)	87.29(16)	93.81(7)	86.71(12)

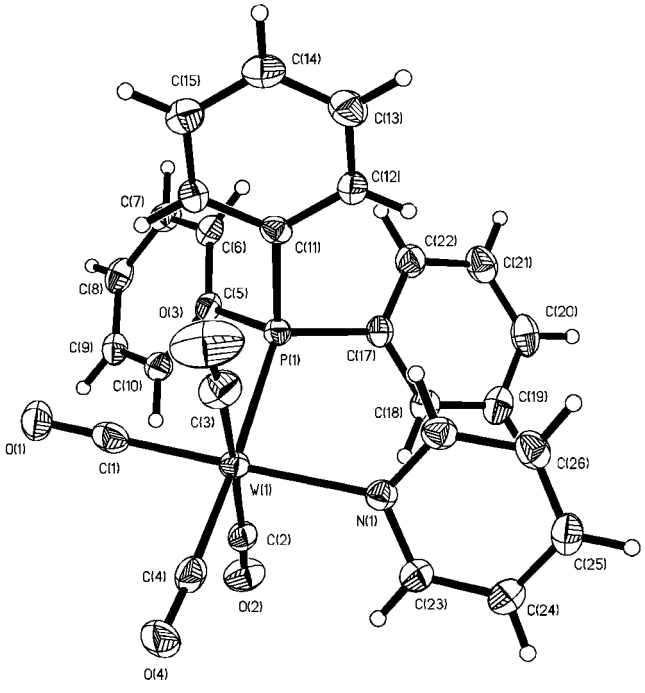


Figure 1. Crystal structure of complex $[W(CO)_4(py)(PPh_3)]$ (**2**)

steric stress to enforce adoption of the *trans* form. The complex $[W(CO)_4\{P(2\text{-py})Ph_2\}_2]$ (**3**, Figure 2) also crystallized in the *cis* form, despite being sterically similar to complex **1**. The structure of *cis*-**3** showed a face-to-face π-stacking interaction between the pyridyl rings, the distance between the centers of the rings being 3.902 Å, and the shortest distance between the atoms of the two rings being 3.527 Å, this being found between the carbon atoms directly attached to the P atom. The planes were found to be almost parallel, having a mutual angle of 7.18(7)°. This interaction is intramolecular rather than extending throughout the crystal system. The centroid–centroid distance between two π-stacked pyridine fragments is typically 3.3–3.8 Å, with contact angles usually falling between a parallel arrangement and a maximum of 40°.[16]

The protonated derivative of **3**, *cis*-$[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}\{P(2\text{-py})Ph_2\}](ClO_4^-)$ (**4**, Figure 3) was found to have a structure in which the N atoms of the pyridyl rings are connected by a hydrogen bond, the distance between the two N atoms being 2.736(3) Å. Because of this hydrogen bond, the positive charge is delocalized over the two pyridine rings. Moreover, the structure of this complex also showed two cation–π bonds between the pyridinium cations and phenyl rings: One such interaction is found between the rings labeled R1 and R3, the centroid–centroid distance of the rings being 3.915 Å with an angle of 23.99°, while the other such interaction is found between the rings labeled R2 and R4, the distance between the centers of the rings being 3.918 Å with an angle of 19.17(15)°. In both cases, the closest distances between the atoms of the rings are found between the N atoms of the pyridyl rings and the C atoms of the phenyl rings directly attached to the P atom, the N1–C distance being 3.179 Å and the N2–C distance being 3.145 Å.

In addition to π-stacking, other weak interactions are also apparent in the solid state. Weak hydrogen bonding between the CO ligands and aryl hydrogen atoms is evident in all the studied complexes. This type of interaction has

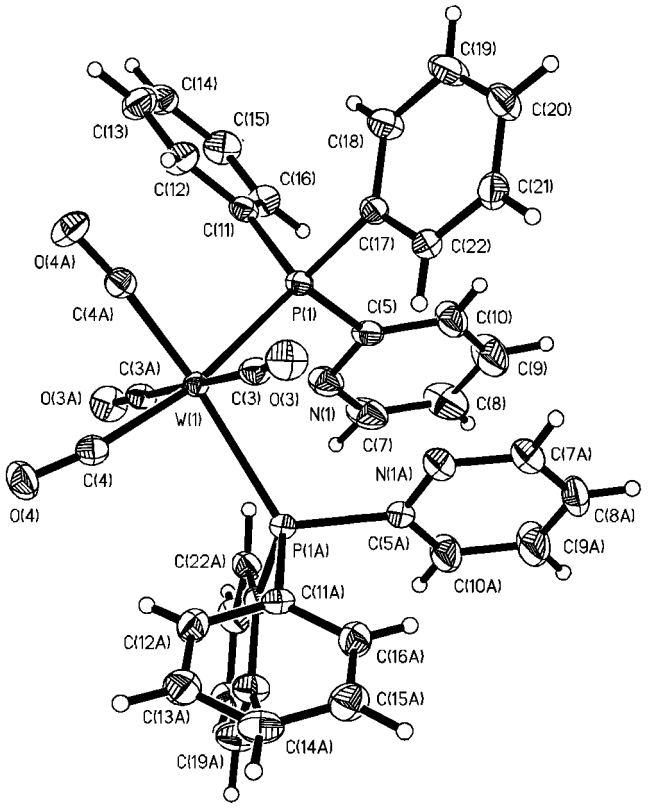


Figure 2. Crystal structure of complex *cis*-$[W(CO)_4\{P(2\text{-py})Ph_2\}_2]$ (**3**)

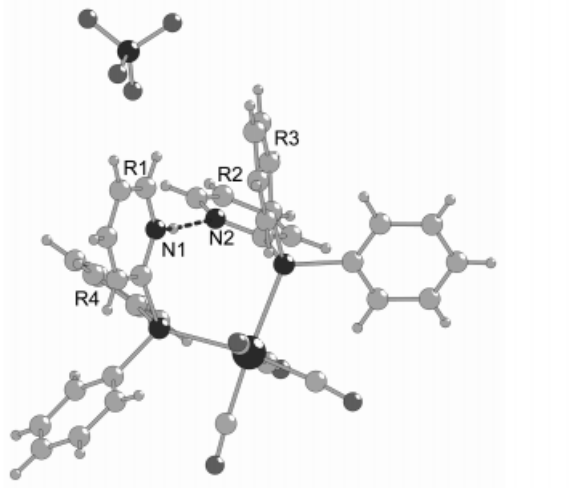
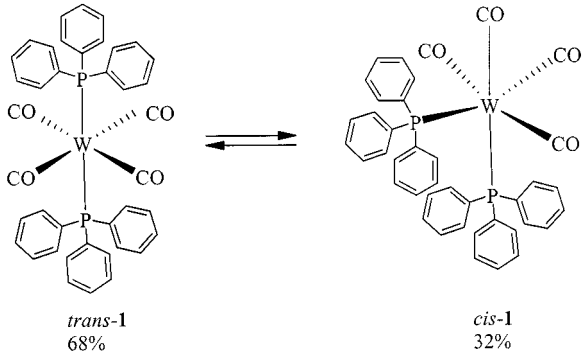


Figure 3. Structure of complex *cis*-$[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}\{P(2\text{-py})Ph_2\}](ClO_4^-)$ (**4**)

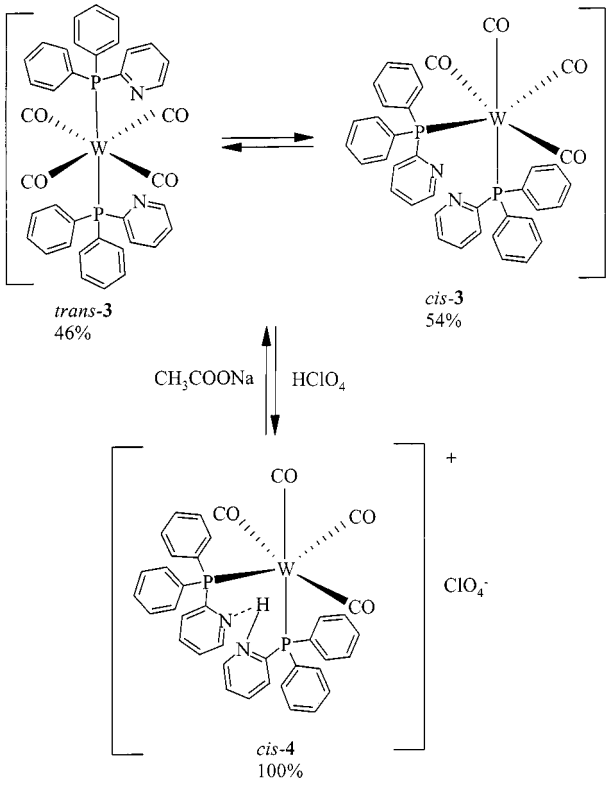
been reported for several carbonyl transition metal complexes.[17] As an example of weak hydrogen bonding in complex **1**, an intermolecular C−O···H distance of 2.529 Å with a C−O···H angle of 172.6° can be seen. Similarly, complex **2** shows an intermolecular C−O···H distance of 2.453 Å with an angle of 161.2°, while complex **3** shows a C−O···H distance of 2.58 Å with a C−O···H angle of 162.4°. Complex **4** shows two C−O···H distances of 2.52 Å with angles of 157.8° and 161.9°. In all of these complexes, this hydrogen-bonding interaction is mainly seen between neighboring molecules in the solid state. These interactions are thus expected to play no significant role in the *cis*/*trans* isomerism in solution.

Discussion

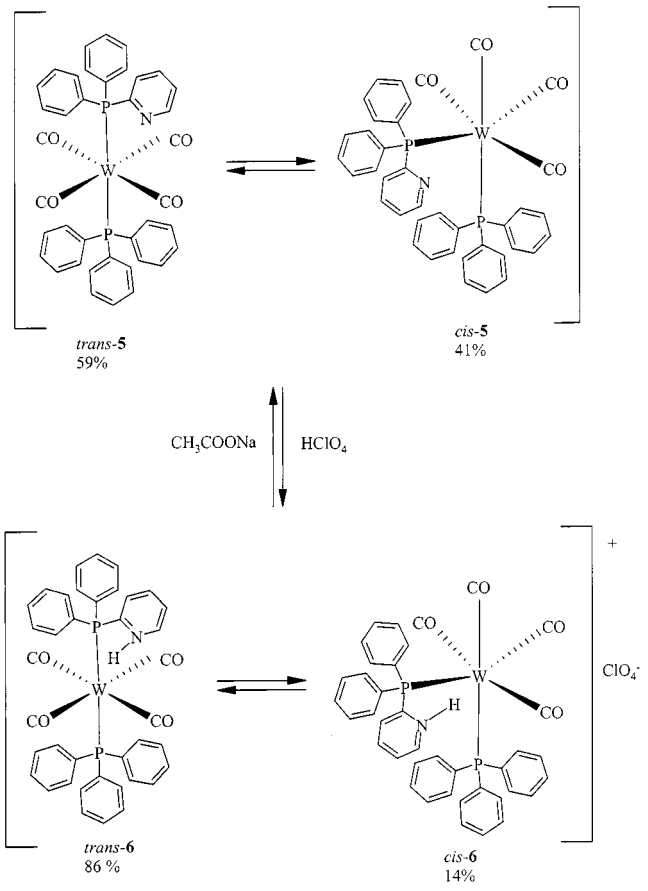
In solution, attractive or repulsive interactions between the ligands have an effect on the isomerization processes. Similar interactions also occur between the ligands and, for example, solvent molecules. The net effect of these interactions, in addition to the electronic properties of the coordination, determines the final structure. In this work, we have deliberately varied the attractions between phosphane ligands in order to cause changes in the relative amounts of the *cis* and *trans* isomers (Schemes 1, 2, and 3).



Scheme 1. Solution behavior of complex **1**



Scheme 2. Solution behavior of complexes **3** and **4**



Scheme 3. Solution behavior of complexes **5** and **6**

The differences in solution behavior of the neutral complexes $[W(CO)_4(PPh_3)_2]$ (**1**), $[W(CO)_4\{P(2\text{-py})Ph_2\}_2]$ (**3**), and $[W(CO)_4(PPh_3)\{P(2\text{-py})Ph_2\}]$ (**5**) can be explained in terms of reduced repulsion between the phosphane ligands due to attractive π−π interactions: Due to the heteroatom, the pyridyl ring is more polarized than the phenyl ring, making attractive π-stacking of pyridyl rings more favorable compared to that of phenyl rings.[18] In the *cis* isomer, showing π−π interactions, the steric repulsion between the ligands is minimized and evidently not much attraction is needed between the rings to favor the *cis* form.

In the case of complex **1**, the steric repulsion between the ligands clearly favors the *trans* isomer. Complex **6** has just one pyridyl ring, which could be involved in attractive π−π interactions with one of the phenyl rings, leading to a slight increase in the *cis* content compared to complex **1**, but the *trans* conformation is still slightly preferred. In complex **3**, the *cis* conformer is favored over the *trans* conformer. In this case, the π-stacking between the pyridyl rings has been confirmed by X-ray crystallography (Figure 2).

The solvent effects are difficult to estimate, but on the grounds of the enthalpies of adduct formation for pyridine (−22 kJ/mol) and benzene (−4.9 kJ/mol) with $CHCl_3$,[19,20] and the empirical solvent polarity parameters of $CHCl_3$ (E_T^N = 0.259), pyridine (E_T^N = 0.302), and benzene (E_T^N = 0.111),[21] pyridine can be expected to show a somewhat greater attraction towards chloroform than benzene. The solvent should actually favor a higher proportion of the *trans* arrangement for complexes **3** and **5** compared to complex **1**, because in the *trans* form the pyridyl groups would maximize their solvent interactions: In the structure of **3** (Figure 2) there are fewer possibilities for solvent interactions with the pyridyl groups. In view of this, the observed isomeric ratios necessitate attractive interactions that override both the steric repulsion of bulky ligands and the solvent interactions.

When complex **3** is protonated, the resulting complex **4** is 100% in the *cis* form. We have isolated the complex $[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}\{P(2\text{-py})Ph_2\}](ClO_4^-)$ (**4**) with one protonated pyridyl ring. This structure offers the possibility of intramolecular N−H···N hydrogen bonding (Figure 3). This hydrogen bond, together with the two cation−π interactions observed, explains the preference for the *cis* isomer.

When complex **5** is protonated, the resulting complex $[W(CO)_4\{P(2\text{-pyH})^+Ph_2\}(PPh_3)](ClO_4^-)$ (**6**) is predominantly (86%) in the *trans* form. Here, there is only one pyridyl ring to bear the positive charge; the possibility still exists for intramolecular cation−π interactions between the pyridinium cation and the phenyl ring, but there is no possibility of intramolecular hydrogen bonding. In this case, the repulsion between the two phosphane ligands becomes important. Additionally, there is a possibility of intermolecular interactions, such as hydrogen bonding between the pyridinium hydrogen atom and the ClO_4^- anion, which may also increase the preference for the *trans* isomer (the *trans* form is even more clearly favored than in the case of the triphenylphosphane derivative **1**). Since the relative strengths of the solvent interactions in complexes **4** and **6** should be comparable, they do not provide an explanation for the structural differences between these two complexes.

The protonation reactions have been found to be reversible; the *cis*/*trans* isomer ratio can be tuned by adjusting the pH. Phosphane complexes are used in various catalytic reactions,[22] hence the ability to control *cis*/*trans* isomerism through attractive interligand interactions opens up possibilities for controlling the mechanisms of homogeneous catalytic reactions.

Experimental Section

General Remarks: All reactions were carried out under nitrogen using standard Schlenk techniques. Synthetic procedures were modified from the method described previously.[14] Benzene (Baker, 99%) was distilled from sodium and benzophenone ketyl under nitrogen. Hexacarbonyltungsten (Aldrich), triphenylphosphane (FF Chemicals), diphenyl(2-pyridyl)phosphane (Aldrich), dichloromethane (FF Chemicals, 99.8%), and hexane (Lab Scan, 95%) were used as received. Perchloric acid (Merck, 70%) was diluted to about 26%. The starting material $[W(CO)_4(py)_2]$ was prepared according to a literature method.[23] Crystals were grown by slow evaporation of the solvents from solutions in dichloromethane/hexane, and in the case of complex **4** from a solution in dichloromethane containing some perchloric acid.

Spectroscopy: ^{1}H NMR spectra (400 MHz; TMS), ^{13}C{^{1}H} NMR spectra (100 MHz; $CDCl_3$ at δ = 77.0), two-dimensional HSQC spectra, and ^{31}P{^{1}H} NMR spectra (162 MHz; ext. stand. 85% H_3PO_4) were recorded with a Bruker DPX 400 spectrometer with samples in $CDCl_3$ (CIL, 99.8% D, 0.03% TMS). IR spectra were recorded with a Bruker IFS 66 spectrometer with samples in dichloromethane. Exact masses were measured with a Micromass LCT mass spectrometer using the ESI+ method.

X-ray Crystallography. − Crystal Data for 2: $C_{27}H_{20}NO_4PW$, M_r = 637.26, monoclinic, a = 10.1507(2), b = 20.0282(3), c = 11.6940(3) Å, β = 97.6790(10)°, 2356.07(8) Å^3, T = 120 K, space group $P2_1/n$ (no. 14), Z = 4, D_{calcd} = 1.797 g cm^{-1}, μ(Mo-$K_α$) = 5.005 mm^{-1}, 25482 reflections collected, 4709 unique (R_{int} = 0.0474). The final R_1 was 0.0235 ($I > 2σ$) and $wR_2(F^2)$ = 0.0564 ($I > 2σ$). − **Crystal Data for 3:** $C_{38}H_{28}N_2O_4P_2W$, M_r = 822.41, monoclinic, a = 13.7402(2), b = 12.6068(2), c = 19.2044(3) Å, β = 96.4360(10)°, 3305.62(9) Å^3, T = 120 K, space group $C2/c$ (no. 15), Z = 4, D_{calcd} = 1.653 g cm^{-1}, μ(Mo-$K_α$) = 3.635 mm^{-1}, 19439 reflections collected, 3622 unique (R_{int} = 0.0238). The final R_1 was 0.0147 ($I > 2σ$) and $wR_2(F^2)$ = 0.0343 ($I > 2σ$). − Data were collected with a Nonius KappaCCD diffractometer using Mo-$K_α$ radiation (λ = 0.71073 Å). For compound **2**, hydrogen atoms were constrained to ride on their parent atom (C−H = 0.95 Å, U_{iso} = 1.2·C_{eq}). In the case of **3**, hydrogen atoms were located from the difference Fourier map and were refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153439 (**2**) and -153440 (**3**). Crystallographic data for the structures reported in a preliminary communication have also been deposited. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[W(CO)$_4$(PPh$_3$)$_2$] (1) and [W(CO)$_4$(py)(PPh$_3$)] (2): [W(CO)$_4$(py)$_2$] (242 mg, 0.533 mmol) was suspended in benzene (40 mL). Triphenylphosphane (151 mg, 0.577 mmol) was added and the mixture was stirred for 24 h at 40−45 °C. The solvent was then evaporated and the residue was purified by column chromatography using dichloromethane/hexane (1:1) as the eluent. Two products, [W(CO)$_4$(PPh$_3$)$_2$] (**1**) (132 mg, 40%) and [W(CO)$_4$(py)(PPh$_3$)] (**2**) (132 mg, 47%) were obtained. − **1**: $C_{40}H_{30}O_4P_2W$ (820.5), calcd. C 58.56, H 3.69; found C 58.32, H 3.20. − *trans*-**1**: ^{1}H NMR: δ = 7.26−7.56 (m). − IR (CH_2Cl_2): ν(CO) = 1886 cm^{-1}. − **2:** Exact mass: m/z = 638.0754 [M$^+$ − H] (calcd. for $C_{27}H_{21}NO_4PW$: 638.0718). − ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.39 (d, 2-H), 7.49 (m, 4-H), 7.36 (m, 12-H), 7.31 (m, 14-H), 7.28 (m, 13-H), 6.82 (t, 3-H). − ^{31}P{^{1}H} NMR: δ = 33 ($^1J_{PW}$ = 238 Hz). − IR (CH_2Cl_2): ν(CO) = 2011 (s), 1884 (vs), 1846 (s) cm^{-1}.

[W(CO)$_4${P(2-py)Ph$_2$}$_2$] (3): [W(CO)$_4$(py)$_2$] (225 mg, 0.495 mmol) was suspended in benzene (40 mL). Diphenyl(2-pyridyl)phosphane (261 mg, 0.991 mmol) was added and the mixture was stirred for 24 h at 40−45 °C. After evaporation of the solvent, the residue was purified by column chromatography using dichloromethane as the eluent to afford [W(CO)$_4${P(2-py)Ph$_2$}$_2$] (225 mg, 55%). Exact mass: m/z = 823.1122 [M$^+$ − H] (calcd. for $C_{38}H_{29}N_2O_4P_2W$: 823.1112). − *cis*-**3:** ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.51 (d, 3-H), 7.45 (m, 8-H), 7.41 (m, 5-H), 7.30 (m, 10-H), 7.26 (m, 9-H), 7.06 (m, 4-H), 7.02 (m, 6-H). − IR (CH_2Cl_2): ν(CO) = 2018 (m), 1911 (sh), 1898 (s), 1872 (sh) cm^{-1}. − *trans*-**3:** ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.78 (d, 3-H), 7.65 (m, 8-H), 7.59 (td, 5-H), 7.36 (m, 9-,10-H), 7.29 (d, 6-H), 7.15 (t, 4-H). − IR (CH_2Cl_2): ν(CO) = 1890 cm^{-1}.

[W(CO)$_4${P(2-pyH)$^+$Ph$_2$}{P(2-py)Ph$_2$}](ClO$_4^-$) (4): Perchloric acid was added to a solution of complex **3** in $CDCl_3$. The product was deprotonated with CH_3COONa solution. − *cis*-**4:** Exact mass: m/z = 823.1109 [M$^+$ − H] (calcd. for $C_{38}H_{29}N_2O_4P_2W$ 823.1112); 98.9509 [ClO_4^-] (calcd. for ClO_4 98.9485). − ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.18 (dd, 3-H), 7.89 (td, 5-H), 7.48 (m, 10-H), 7.47 (m, 9-H), 7.38 (m, 4-H), 7.34 (m, 8-H), 7.23 (dd, 6-H).

[W(CO)$_4${P(2-Py)Ph$_2$}(PPh$_3$)] (5): [W(CO)$_4$(py)(PPh$_3$)] (**2**, 110 mg, 0.173 mmol), obtained in the preparation of complex **1** as described above, was dissolved in benzene (20 mL) and diphenyl(2-pyridyl)-phosphane (55 mg, 0.209 mmol) was added. The resulting solution was stirred for 24 h at 40−50 °C and then the solvent was evaporated. The product was purified by column chromatography, first with dichloromethane/hexane (1:1) as eluent until the first fraction (starting material and traces of complex **1**) eluted, and thereafter with a 1:3 mixture until the product was eluted. Exact mass: m/z = 822.1194 [M$^+$ − H] (calcd. for $C_{39}H_{30}NO_4P_2W$: 822.1160). − *cis*-**5:** ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.55 (dd, 3-H), 7.59 (m, 8-H), 7.45 (m, 5-H), 7.42−7.25 (m, 10-H), 7.30−7.20 (m, 9-H, 11- to 14-H), 7.08 (m, 4-H), 6.97 (m, 6-H). − *trans*-**5:** ^{1}H NMR (see Table 1 for numbering scheme): δ = 8.80 (dd, 3-H), 7.67 (m, 8-H, 11- to 14-H), 7.59 (m, 5-H), 7.45−7.35 (m, 9-H), 7.42−7.25 (m, 10-H), 7.29 (m, 6-H), 7.16 (m, 4-H). − IR (CH_2Cl_2): ν(CO) = 1888 cm^{-1}.

[W(CO)$_4${P(2-pyH)$^+$Ph$_2$}(PPh$_3$)](ClO$_4^-$) (6): Perchloric acid was added to a solution of complex **5** in $CDCl_3$. The product **6** was deprotonated with CH_3COONa solution. The protonated complex showed a tendency to decompose if the solution was left to stand over a period of days. − *trans*-**6:** Exact mass: m/z = 822.1164 [M$^+$ − H] (calcd. for $C_{39}H_{30}NO_4P_2W$: 822.1160); 98.9510 [ClO_4^-] (calcd. for ClO_4 98.9485). − ^{1}H NMR (see Table 1 for numbering scheme): δ = 9.16 (dd, 3-H), 7.90−7.20 (m, 4- to 14-H).

Acknowledgments

Financial support from the Neste foundation is gratefully acknowledged. We thank Mrs. Päivi Joensuu for recording the mass spectra, and Mrs. Päivi Pirilä for advice in the area of solution chemistry.

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Received March 2, 2001
[I01080]