# 40. Reduction of Aldehydes and Ketones by Transition Metal Hydrides

Part 2[1])

## Reaction of *trans,trans*-[WH(CO)$_2$(NO)(PMe$_3$)$_2$] with Pyridine, Functionalized Aldehydes, and Ketones

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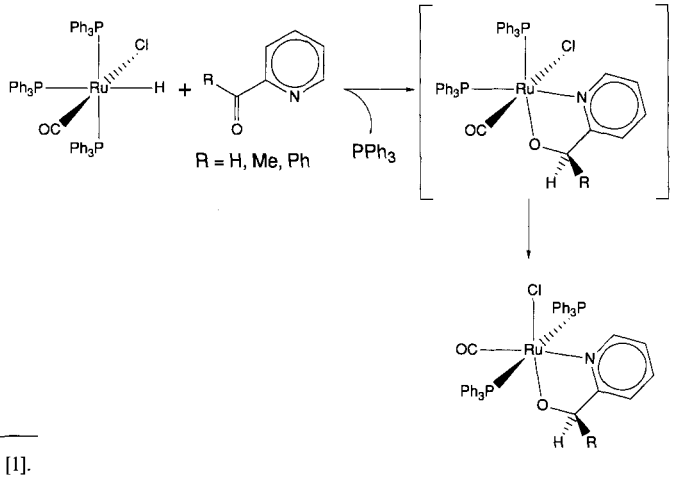
The reaction of *trans,trans*-[WH(CO)$_2$(NO)(PMe$_3$)$_2$] (**1**) with (pyridin-2-yl)-substituted aldehydes and ketones, (pyridin-2-yl)C(O)R where R = H, Me, Ph, pyridin-2-yl, and with 6-methylpyridine-2-carbaldehyde was studied. In all cases, facile insertion of the C=O bond into the W–H bond was observed, with rapid subsequent extrusion of a coordinated CO ligand affording *O,N*-bidentate coordinated tungsten alkoxides. Only in case of pyridine-2-carbaldehyde and di(pyridin-2-yl) ketone, the initial $\eta^1$ O-bonded insertion product could be observed as unstable intermediates by low-temperature NMR.

**Introduction.** – In a previous paper, we reported the facile insertion of simple aldehydes into the W–H bond of *trans,trans*-[WH(CO)$_2$(NO)(PMe$_3$)$_2$] (**1**), affording tungsten alkoxides [1]. However, attempts to isolate these insertion products were unsuccessful due to subsequent decomposition. This instability was ascribed to the labilizing effect of the alkoxide groups on the metal carbonyl bonds [2]. To study these insertion reactions and products in greater detail, we, therefore, contemplated the use of modified aldehydes and

*Scheme 1*




[1]) Part 1: [1].

ketones, that contain additional chelating functionalities for 'trapping' the primary insertion product in this way. As far as we know, there is only one example for such an approach to be found in the literature involving a ruthenium hydride (see *Scheme 1*) [3]. In this paper, we report the results of similar reactions of **1** with (pyridin-2-yl)-substituted aldehydes and ketones.

**Experimental.** – *General.* All preparations were carried out under dry $N_2$ by conventional *Schlenk* techniques. All of the described reaction products, however, could be handled in air. Solvents were dried and freshly distilled before use. *trans,trans*-$[WH(CO)_2(NO)(PMe_3)_2]$ (**1**) was prepared as described in [4]. The required pyridine derivatives were commercially available (*Fluka AG*). IR spectra were recorded as a toluene soln. on a *Biorad FTS-45* instrument. $^1$H- and $^{13}$C-NMR spectra were run on a *Varian Gemini-200* operating at 200 and 50.3 MHz, respectively, $^{31}$P-NMR spectra on a *Varian XL-200* spectrometer at 81 MHz. Mass spectra (EI) were run on a *Finnigan MAT-8230* mass spectrometer; the major peaks given are based on $^{184}$W.

trans-$[\overline{W[NC_5H_4(2\text{-}CH_2O)]}(CO)(NO)(PMe_3)_2]$ (**2b**): *Method A.* To a soln. of **1** (0.19 g, 0.45 mmol) in 4 ml of toluene was added 50 µl (1.1 equiv.) of pyridine-2-carbaldehyde at r.t. After 10 min, solvent was removed *in vacuo*, yielding an orange residue, which, after washing with hexane, contained pure **2b** in 95% yield. MS: 502 ($M^+$), 474 ([$M$ – CO]$^+$), 426 ([$M$ – $PMe_3$]$^+$), 398 ([$M$ – CO, $PMe_3$]$^+$), 322 ([W – CO, 2$PMe_3$]$^+$). Anal. calc. for $C_{13}H_{24}N_2O_3P_2W$: C 31.11, H 4.82, N 5.58; found: C 31.11, H 5.07, N 5.35.

*Method B.* An equimolar mixture of **1**, propanal, and (pyridin-2-yl)methanol in toluene was stirred for 1 h at r.t. Workup as described above afforded **2b** in 90% yield.

trans-$[\overline{W[NC_5H_3(6\text{-}Me)(2\text{-}CH_2O)]}(CO)(NO)(PMe_3)_2]$ (**3**). As described for **2b**. Reaction time 4 h at 50°. Yield: 90%. MS: 516 ($M^+$), 488 ([$M$ – CO]$^+$), 440 ([$M$ – $PMe_3$]$^+$), 412 ([$M$ – CO, $PMe_3$]$^+$), 336 ([W – CO, 2 $PMe_3$]). Probably due to its thermal instability, no acceptable elemental analysis for **3** could be obtained.

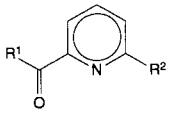
trans-$[\overline{W[NC_5H_4(2\text{-}CH(Me)O)]}(CO)(NO)(PMe_3)_2]$ (**4a**) *and* trans-$[\overline{W[NC_5H_4(2\text{-}C(=CH_2)O)]}(CO)(NO)(PMe_3)_2]$ (**4b**). A mixture of **1** (0.15 g, 0.36 mmol) and methyl pyridin-2-yl ketone (0.40 ml, 10 equiv.) in 10 ml of toluene was stirred for 6 d at 50° *in vacuo*. The soln. was concentrated and chromatographed over silica gel. Elution with THF/hexane 1:1 afforded an orange band, which, after recrystallization from hexane, afforded 20 mg (10%) of orange-red crystals of **4b**. MS: 514 ($M^+$), 486 [$M$ – CO]$^+$), 438 ([$M$ – $PMe_3$]$^+$), 410 ([$M$ – CO, $PMe_3$]$^+$). Anal. calc. for $C_{14}H_{24}N_2O_3P_2W$: C 32.71, H 4.71; found: C 32.92, H 4.93.

Further elution with increasing amounts of THF afforded a second orange band, which, after recrystallization from hexane, consisted of pure **4a** (70 mg, 40%). MS: 516 ($M^+$), 488 ([$M$ – CO]$^+$), 440 ([$M$ – $PMe_3$]$^+$), 412 ([$M$ – CO, $PMe_3$]$^+$), 382 ([$M$ – CO, NO, $PMe_3$]$^+$), 336 ([W – CO, 2$PMe_3$]$^+$). Anal. calc. for $C_{14}H_{26}N_2O_3P_2W$: C 32.58, H 5.08; found: C 31.91, H 4.90.

trans-$[\overline{W[NC_5H_4(2\text{-}CH(Ph)O)]}(CO)(NO)(PMe_3)_2]$ (**5**). As described for **2b**. Reaction time 24 h at 50°. Yield: 80%. MS: 578 ($M^+$), 550 ([$M$ – CO]$^+$), 502 ([$M$ – $PMe_3$]$^+$), 474 ([$M$ – CO, $PMe_3$]$^+$), 398 ([W – CO, 2$PMe_3$]$^+$). Anal. calc. for $C_{19}H_{28}N_2O_3P_2W$: C 39.47, H 4.88; found: C 38.81, H 4.58.

The reaction of **1** with di(pyridin-2-yl) ketone was followed by NMR. No tractable compounds could be isolated from this reaction.

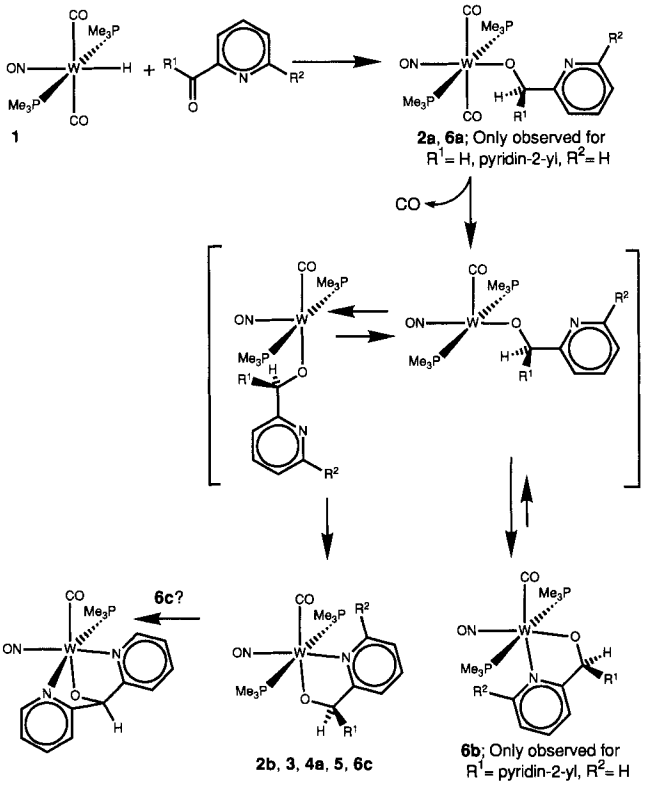
**Results.** – The reactions of **1** with the following pyridine derivatives were investigated:




| $R^1$ | $R^2$ | Reaction products |
|---|---|---|
| H | H | **2a, 2b** |
| H | Me | **3** |
| Me | H | **4a, 4b** |
| Ph | H | **5** |
| Pyridin-2-yl | H | **6a, 6b, 6c, ...** |

In all cases, insertion of the C=O bond into the W–H bond of **1** was observed. The reaction rate varies considerably and follows the order **6** > **2** > **3** ≈ **5** > **4**. All reaction were monitored by (low-temperature) NMR in order to trap any possible intermediate,

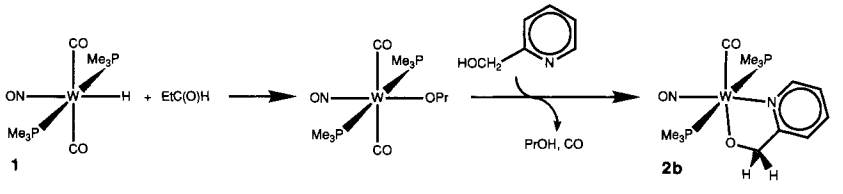
*Scheme 2*




that could have been formed (see *e.g.* **6** in the *Figure*). All reactions seem to proceed *via* initial formation of an $\eta^1$-bonded tungsten alkoxy compound (see *Scheme 2*), although only for **2** and **6** the intermediacy of such a product was actually confirmed. In all cases subsequent loss of CO took place with formation of *O,N*-chelated insertion products. The isostructural compouds **2b**, **3**, **4a**, and **5** could be isolated. The characteristics of each reaction will now be presented.

The reaction of **1** with pyridine-2-carbaldehyde started at −10° (NMR monitoring in ($D_8$)THF), affording the initial product **2a**. Loss of CO occurred shortly afterwards at *ca.* 10° cleanly producing **2b**, which could be isolated on a preparative scale in 95% yield. The

*Scheme 3*

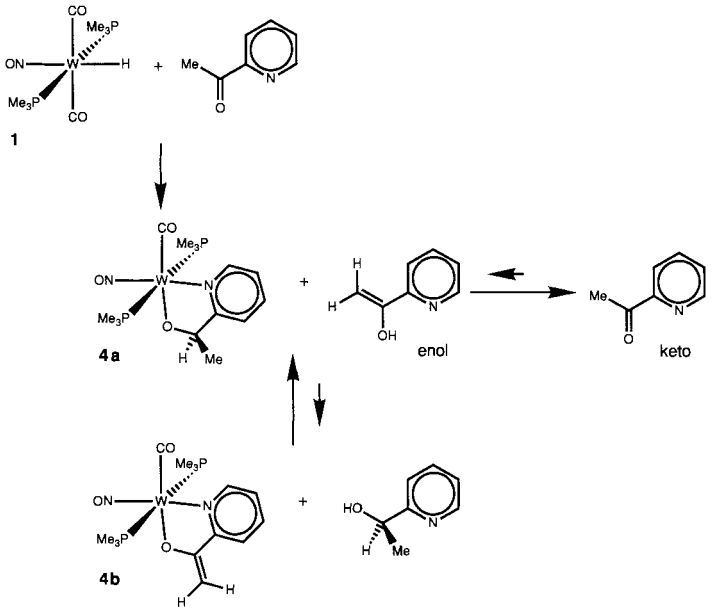


reaction with $(D_1)$-**1** afforded $(D_1)$-**2b** in which the D is exclusively on the alkoxy C atom ($^{13}$C-NMR ($C_6D_6$): 75.3 ppm (*t*, $^1J$(C,D) = 21.2 Hz, O*C*(D)H)). As an alternative, **2b** may be prepared from the reaction of *trans,trans*-[W(OPr)(CO)$_2$(NO)(PMe$_3$)$_2$] (prepared *in situ via* reaction of propanal with **1**) [1], and subsequent substitution by (pyridin-2-yl)methanol (*Scheme 3*).

The reaction of **1** with the 6-Me-substituted derivative was surprisingly slow (4 h at 50°), as compared to the preceding one. An intermediate analogous to **2a** was not observed, and **3** (isostructural to **2b**) was isolated in very good yield. This compound, however, is thermally rather unstable, probably due to steric interference between the 6-Me group and the adjacent W-coordinated ligands.

The reaction of **1** with methyl pyridin-2-yl ketone is very slow (days at 50°), and is complicated by the fact that the initial insertion product **4a** partly reacts further with excess methyl pyridin-2-yl ketone (as its enol form) to the tungsten enolate complex **4b** and 1-(pyridin-2-yl)ethanol (*Scheme 4*)[2]). Both W complexes could, however, be separated and isolated after chromatography.

*Scheme 4*




After a reaction time of 24 h at 50°, **1** and phenyl pyridin-2-yl ketone yielded **5** as the sole product.

The reaction between **1** and di(pyridin-2-yl) ketone was followed by NMR only (*Fig.*), since all attempts to isolate the products were unsuccessful. This reaction was extremely fast, compared to the isosteric phenyl pyridin-2-yl ketone. Thus, reaction already oc-

[2]) $^1$H-NMR ($C_6D_6$) of 1-(pyridin-2-yl)ethanol: 1.55 (*d*, *J* = 6.5, $CH_3$); 5.00 (*q*, *J* = 6.5, C*H*CH$_3$); arom. H's hidden. $^{13}$C-NMR ($C_6D_6$): 24.7 ($CH_3$); 69.5 (C*H*CH$_3$); 119.8 (C(5')); 121.7 (C(3')); 136.4 (C(4')); 148.4 (C(6')); C(2') not observed.

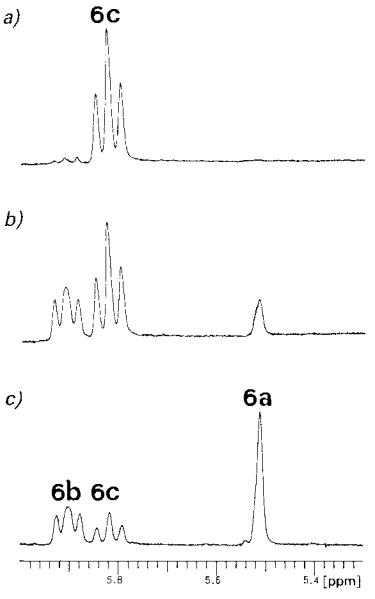



Figure. *Reaction of* **1** (0.17 mmol) *and di(pyridin-2-yl) ketone* (0.17 mmol) *in* $(D_8)THF$ (0.6 ml) *started at* $-50°$. Only the region of the $^1$H-NMR spectrum where the alkoxy H's resonate is shown: *a*) $-20°$; *b*) $-5°$; c) $-5°$ after 1 h.

curred at $-20°$ in $(D_8)$THF, affording the insertion product **6a**, which, on spectroscopic grounds (*vide infra*), is isostructural to **2a**. A small raise in temperature soon caused the disappearance of **6a**, with formation of two new compounds, **6b** and **6c**. Compound **6b**, however, is observable only within a very narrow temperature range, as it was readily converted to **6c**. The transient species **6b** seems to be the CO/NO exchanged isomer of **6c**, *vide infra*. Compound **6c** was the only compound present between *ca.* $-10$ and $+10°$; it is structurally analogous to **2b**, **3**, **4a**, and **5**. At room temperature, **6c** slowly decomposed with loss of $PMe_3$, probably producing a species in which the alkoxy ligand is *O,N,N'*-tridentate-coordinated to W, however, further decomposition precluded its full characterization[3]).

**Identification of Compounds.** – Elemental analyses and mass spectra of the isolated compounds **2b**, **3**, **4a**, **4b**, and **5** were all in accord with the presumed composition of the insertion products; their structures and those of **2a**, **6a**, **6b**, and **6c** were determined by a combination of IR (*Table 1*), and $^1$H-, and $^{13}$C-, and $^{31}$P-NMR spectroscopy (*Table 2*).

Table 1. *IR Data*[a])

| Compound | $\nu$(CO) | $\nu$(NO) | Compound | $\nu$(CO) | $\nu$(NO) |
|---|---|---|---|---|---|
| **2b** | 1881 | 1544 | **4b** | 1886 | 1550 |
| **3** | 1884 | 1551 | **5** | 1881 | 1545 |
| **4a** | 1879 | 1542 | **6c** | 1879 | 1546 |

[a]) In $cm^{-1}$. The CO band is very intense, that of NO is of moderate intensity. IR spectra were measured in toluene at room temperature.

[3]) $^1$H-NMR ($(D_8)$THF): 1.38 (*d*, $^2J$(H,P) = 8.6, P($CH_3$)$_3$); 6.50 (*s*, OCH). $^{13}$C-NMR ($(D_8)$THF): 18.0 (*d*, $^2J$(C,P) = 70.2, P($CH_3$)$_3$); 85.6 (OCH). $^{31}$P-NMR ($(D_8)$THF): $-7.7$ ($^1J$(P,W) = 407).

Table 2. *$^1$H-, $^{13}$C-, and $^{31}$P-NMR Data*[a])

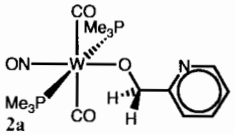
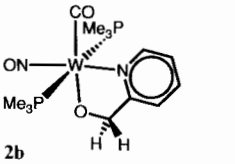
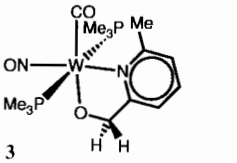
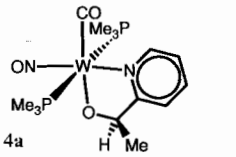
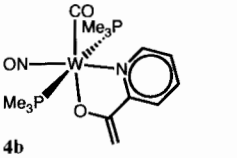
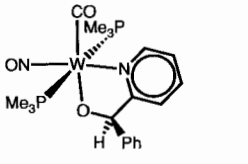
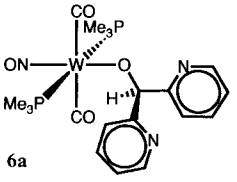
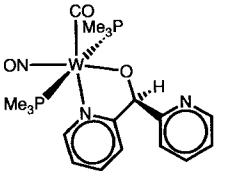
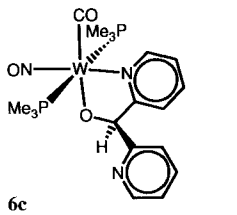
| | | |
|---|---|---|
|  **2a** | $^1$H ($(D_8)$THF, −25°) | 1.64 (*t*, $^{2,4}J$(H,P) = 3.6, $P(CH_3)_3$); 4.64 ($CH_2O$); 7.27 (*m*, H−C(3′)); 7.55 (*m*, H−C(4′)); 6.99 (*m*, H−C(5′)); 8.34 (*m*, H−C(6′)). |
| | $^{13}$C | 17.3 (*t*, $^{1,3}J$(C,P) = 14.1, $P(CH_3)_3$); 77.6 ($CH_2$); 212.2 (*t*, $^2J$(C,P) = 6.5, W−CO); 168.8 (C(2′)); 121.6 (C(3′)); 136.5 (C(4′)); 120.6 (C(5′)); 149.2 (C(6′)). |
|  **2b** | $^1$H ($C_6D_6$, 21°) | 1.05 (*t*, $^{2,4}J$(H,P) = 3.2, $P(CH_3)_3$); 5.10 (*t*, $^4J$(H,P) = 3.9, $CH_2O$); 6.44 (*d*, *J* = 7.8, H−C(3′)); 6.79 (*t*, *J* = 7.6, H−C(4′)); 6.37 (*t*, *J* = 6.5, H−C(5′)); 8.79 (*d*, *J* = 5.4, H−C(6′)). |
| | $^{13}$C | 14.8 (*t*, $^{1,3}J$(C,P) = 11.9, $P(CH_3)_3$); 75.8 ($CH_2$); 245.1 (*t*, $^2J$(C,P) = 4.2, W−CO); 169.2 (C(2′)); 121.8 (C(3′)); 135.4 (C(4′)); 118.2 (C(5′)); 147.4 (C(6′)). |
| | $^{31}$P | −16.3 ($^1J$(P,W) = 308). |
|  **3** | $^1$H | 1.03 (*t*, $^{2,4}J$(H,P) = 3.2, $P(CH_3)_3$); 2.76 (aryl $CH_3$); 5.11 (*t*, $^4J$(H,P) = 3.3, $CH_2O$); 6.35 (*d*, *J* = 8.0, H−C(3′)); 6.76 (*t*, *J* = 7.5, H−C(4′)); 6.39 (*d*, *J* = 7.4, H−C(5′)). |
| | $^{13}$C | 15.0 (*t*, $^{1,3}J$(C,P) = 11.9, $P(CH_3)_3$); 27.4 (aryl $CH_3$); 76.6 ($CH_2$); 242.2 (*t*, $^{2,4}J$(C,P) = 4.1, W−CO); 169.6 (C(2′)); 122.0 (C(3′)); 135.4 (C(4′)); 115.0 (C(5′)); 160.7 (C(6′)). |
| | $^{31}$P | −16.0 ($^1J$(P,W) = 305). |
|  **4a** | $^1$H | 1.05 (*m*, $P(CH_3)_3$); 1.31 (*d*, *J* = 6.5, >C(H)$CH_3$); 4.84 (br. *q*, *J* = 6.5, OC(H)); 6.48 (*d*, *J* = 8.0, H−C(3′)); 6.81 (*t*, *J* = 7.6, H−C(4′)); 6.38 (*t*, *J* = 6.4, H−C(5′)); 8.81 (*d*, *J* = 5.3, H−C(6′)). |
| | $^{13}$C | 14.4, 15.3 (*m*, $P(CH_3)_3$); 25.6 (>C(H)$CH_3$); 79.2 (>C(H)$CH_3$); 245.3 (br., W−CO); 171.3 (C(2′)); 122.2 (C(3′)); 136.0 (C(4′)); 120.3 (C(5′)); 147.1 (C(6′)). |
| | $^{31}$P | −17.0 ($^1J$(P,W) = 300); −17.4 ($^1J$(P,W) = 306) (*AB doublets* with $^2J$(P,P) = 236). |
|  **4b** | $^1$H | 1.00 (*t*, $^{2,4}J$(H,P) = 3.4, $P(CH_3)_3$); 4.61, 4.68 (br. *s*, >C = $CH_2$); 7.09 (*d*, *J* = 8.2, H−C(3′)); 6.70 (*t*, *J* = 7,6, H−C(4′)); 6.30 (*t*, *J* = 6.5, H−C(5′)); 8.68 (*d*, *J* = 5.5, H−C(6′)). |
| | $^{13}$C | 14.4 (*t*, $^{1,3}J$(C,P) = 12.0, $P(CH_3)_3$); 85.5 (>C = $CH_2$); W−CO and >C = $CH_2$ not observed; 166.1 (C(2′)); 122.4 (C(3′)); 135.3 (C(4′)); 120.6 (C(5′)); 146.7 (C(6′)). |
| | $^{31}$P | −13.7 ($^1J$(P,W) = 303). |
|  **5** | $^1$H ($(D_8)$THF, 21°) | 1.24 (*dd*, *J* = 4.1, 2.3, $P(CH_3)_3$); 1.33 (*dd*, *J* = 3.9, 2.2, $P(CH_3)_3$); 5.61 (*t*, $^4J$(H,P) = 4.8, OCH); 6.94 (*d*, *J* = 7.9, H−C(3′)); 7.64 (*t*, *J* = 7.6, H−C(4′)); 7.25? (H−C(5′)); 8.84 (*d*, *J* = 5.3, H−C(6′)); 7.25 (Ph H's). |
| | $^1$H ($C_6D_6$, 21°) | 1.09 (*dd*, *J* = 4.3, 2.0, $P(CH_3)_3$); 1.14 (*dd*, *J* = 4.2, 2.0, $P(CH_3)_3$); 5.61 (*t*, $^4J$(H,P) = 4.8, OCH); 6.50 (*d*, *J* = 7.9, H−C(3′)); 6.71 (*t*, *J* = 7.6, H−C(4′)); 6.39 (*t*, *J* = 6.4, H−C(5′)); 8.85 (*d*, *J* = 5.4, H−C(6′)); 7.2 (*m*, Ph H's). |
| | $^{13}$C | 14.7, 15.7 (*dd*, *J* = 13.8, 9.5, $P(CH_3)_3$); 87.5 (OCH); 244.7 (*t*, $^2J$(C,P) = 4.2, W−CO); 168.8 (C(2′)); 121.6 (C(3′)); 135.5 (C(4′)); 122.1 (C(5′)); 147.5 (C(6′)); 128.2 (2×), 131.6, 147.3 (Ph). |
| | $^{31}$P | −17.0 ($^1J$(P,W) = 306); −17.1 ($^1J$(P,W) = 299) (*AB d*'s with $^2J$(P,P) = 227). |

*Table 2* (cont.)

| | | |
|---|---|---|
|  **6a** | $^1$H ((D$_8$)THF, −20°) | 1.51 ('*t*', $^{2,4}J$(H,P) = 3.6, P(CH$_3$)$_3$); 5.51 (OCH); 7.32 (*ddd*, H–C(3'), H–C(3")); 7.57 (*ddd*, H–C(4'), H–C(4")); 7.04 (*ddd*, H–C(5'), H–C(5")); 8.35 (*ddd*, H–C(6'), H–C(6")); with $^3J$(3',4') = 7.8, $^4J$(3',5') = 1.4, $^5J$(3',6') = 0.7, $^3J$(4',5') = 7.5, $^4J$ = 7.5, $^4J$(4,6') = 1.8, $^3J$(5',6') = 4.8. |
| | $^{13}$C | 17.4, ('*t*', $^{1,3}J$(C,P) = 13.9, P(CH$_3$)$_3$); 89.2 (OCH); 211.2 (*t*, $^2J$(C,P) = 6.5, W–CO); 168.3 (C(2'), C(2")); 122.3 (C(3'), C(3")); 136.5 (C(4'), C(4")); 122.2 (C(5'), C(5")); 149.2 (C(6'), C(6")). |
| | $^{31}$P | −24.3 ($^1J$(P,W) = 295). |
|  **6b** | $^1$H ((D$_8$)THF, −20°) | 1.28 (*dd*, *J* = 6.1, 9.0, P(CH$_3$)$_3$); 5.90 (*t*, $^4J$(H,P) = 4.8, OCH); 7.87 (*t*, *J* = 7.5, H–C(3')); 8.44 (*d*, *J* = 5.6, H–C(6')); 8.52 (*ddd*, $^3J$(5",6") = 4.9, $^4J$(4",6") = 1.9, $^5J$(3",6") = 1.0, H–C(6")); resonances of H–C(4'), H–C(5'), H–C(3"), H–C(4"), and H–C(5") are obscured. |
| | $^{13}$C | 14.8 (*dd*, *J* = 19.5, 5.1, P(CH$_3$)$_3$); 16.4, (*dd*, *J* = 19.5, 6.2, P(CH$_3$)$_3$); 87.7 (OCH); 262.2 (*t*, $^2J$(C,P) = 3.1, W–CO); 168.7, 174.3 (C(2'), C(2")); 124.0 (2×?, C(3'), C(3")); 136.4, 138.8 (C(4'), C(4")); 122.1, 123.1 (C(5'), C(5")); 149.0, 150.3 (C(6'), C(6")). |
| | $^{31}$P ((D$_8$)THF, −5°) | −14.2 ($^1J$(P,W) = 306); −15.1 ($^1J$(P,W) = 294) (*AB d*'s with $^2J$(P,P) = 220). |
|  **6c** | $^1$H | 1.20 (*dd*, *J* = 4.5, 1.9, P(CH$_3$)$_3$); 1.30 (*dd*, *J* = 4.6, 2.0, P(CH$_3$)$_3$); 5.82 (*t*, $^4J$(H,P) = 4.9, OCH); 7.58 (*t*, *J* = 7.7, H–C(3')); 8.80 (*d*, *J* = 5.3, H–C(6')); 8.47 (*ddd*, $^3J$(5",6") = 4.8, $^4J$(4",6") = 1.8, $^5J$(3",6") = 0.9, H–C(6")); 7.15 (*ddd*, $^3J$(5",6") = 4.7, $^3J$(4",5") = 7.3, $^4J$(3",6") = 1.5, H–C(3")); resonances of H–C(4"), H–C(5'), H–C(4"), and H–C(5") are obscured. |
| | $^{13}$C | 15.1 (*dd*, *J* = 15.4, 8.9, P(CH$_3$)$_3$); 15.8 (*dd*, *J* = 15.2, 9.3, P(CH$_3$)$_3$); 87.6 (OCH); 246.1 (*t*, $^2J$(C,P) = 4.0, W–CO); 167.3, 168.8 (C(2'), C(2")); 123.6, 123.8 (C(3'), C(3")); 137.1, 137.2 (C(4'), C(4")); 122.8 (2×, C(5'), C(5")); 148.0, 149.2 (C(6'), C(6")). |
| | $^{31}$P | −17.5 ($^1J$(P,W) = 299); −17.7 ($^1J$(P,W) = 304) (*AB d*'s with $^2J$(P,P) = 233). |

[a]) The C-atoms in the pyridine moieties are indicated by primed (and doubly primed) numbers (C(2'), C(2"), *etc.*). Assignment of aromatic H- and C-atoms was accomplished with help of $^1$H spin-decoupling and off-resonance-decoupling $^{13}$C experiments; however, the $^{13}$C resonances of C(3') and C(5') may be interchanged. *J* in [Hz].

The isostructural compounds **2a** and **6a** were identified by $^1$H- and $^{13}$C-NMR only. The coordinated CO ligands show corresponding $^{13}$C resonances at 212.2 and 211.2 ppm, respectively, and $^{31}$P coupling constants (6.5 Hz for both) that are typical of a *trans,trans*-[WX(CO)$_2$(NO)(PMe$_3$)$_2$] arrangement [1] [4]. Compound **6a** shows only one set of resonances for the two pyridine moieties, consistent with the assumption that they are both not (yet) coordinated to the W-atom. Furthermore, it was noticed that the $^1$H resonances of the alkoxy moiety (at 4.64 ppm for **2a**, and 5.51 ppm for **6a**) do not show a resolvable

coupling to the P-atom, in contrast to those of the *O,N*-chelated compounds **2b**, **3**, **4a**, **5**, **6b**, and **6c**.

Those chelated compounds that arise from insertion of an aldehyde, *i.e.* **2b** and **3**, as well as **4b**, possess a mirror plane within the molecule, and those originating from insertion of a ketone, *i.e.* **4a**, **5**, **6b**, and **6c** have a chiral C-atom and hence lack any form of symmetry. This is nicely seen in the NMR spectra of these compounds, which show one $^1$H, $^{13}$C, and $^{31}$P resonance for the two *trans*-positioned $PMe_3$ groups in the former case and two resonances for the latter (with $^2J$(P,P) in the range 220–236 Hz). An *O,N*-chelating coordination mode of the alkoxy ligand is anticipated also on the basis of electron and ligand count.

The enolate structure of **4b** is clearly deduced from its mass spectrum, as well as from the observation of two olefinic signals in the $^1$H-NMR spectrum. Its IR spectrum indicates that the coordination sphere is identical to that of the series **2b**, **3**, **4a**, **5**, and **6c**.

The NMR data of the *O,N*-chelated compounds **2b**, **3**, **4a**, **4b**, **5**, and **6c** confirm the mutual *trans*-position of two $PMe_3$ ligands. The alkoxy moiety must, therefore, be in a plane that is perpendicular to the P–W–P axis and, as its O- and N-atoms are forced in a *cis*-position, two possibilities concerning the positions of the CO and NO ligands remain. The IR absorptions of these ligands both fall into narrow ranges and suggests that all of these compounds are isostructural in this sense. Comparison of the $\nu$(CO) and $\nu$(NO) data as well as the $^{13}$C-NMR data (W–*C*O) with other data[4][5] suggests that the CO ligand must be *trans*-positioned to an O-atom and the NO ligand *trans*-positioned to the pyridine N-atom. This assignment was confirmed by a heteronuclear NOE-difference experiment on **2b**. Thus, irradiating the $^1$H resonance at 8.79 ppm, which was attributed to H–C(6) of the pyridine moiety, caused a 10% increase of the intensity of the $^{13}$C resonance at 245.1 ppm, which was assigned to the W–*C*O C-atom. This means that the CO ligand must be *cis*-positioned to the pyridine moiety and hence *trans*-positioned to the alkoxy O-atom (in this arrangement the distance between the two nucleii involved is estimated to be 3.3 Å by molecular modelling).

It is believed that the transient species **6b** is the CO/NO exchanged isomer of **6c**. Thus, the NMR data for the $PMe_3$ ligands confirm their mutual *trans*-arrangement ($^2J$(P,P′) = 220 Hz). The $^1$H and $^{13}$C resonances of the organic moiety suggest the presence of a coordinated and an uncoordinated pyridine ring, as in **6c**, and the $^4J$(H,P) coupling of 4.8 Hz on the alkoxy H-atom (compare 4.9 Hz in **6c**) corroborates the *O,N*-chelating mode of coordination. Finally, the $^{13}$C resonance of the CO ligand (262.2 ppm) would be typical of a *trans*-*N*-coordinated arrangement [6].

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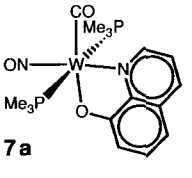
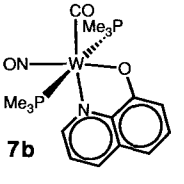
[4]) The $^{13}$C chemical shifts of CO in compounds of the type *trans*-[W(X)(Y)(CO)(NO)($PMe_3$)$_2$] (X, Y is any C, N, O $\sigma$-donor atom) are always found in the region of 240 to 260 ppm. Specific spectroscopic data for *trans*-O–W–CO and *trans*-O–W–NO moieties are: $^{13}$C-NMR: 240–250. IR: 1880–1890 (CO); 1575–1605 (NO) [1] [5].

[5]) The IR (in toluol) and $^{13}$C-NMR (in $C_6D_6$) data may be compared to those of the related isomers **7a** ($\nu$(CO) = 1888, $\nu$(NO) = 1565 cm$^{-1}$; $\delta$(W–*C*O): 244.3 (*t*, $^2J$(C,P) = 4.0 Hz) ppm) and **7b** ($\nu$(CO) = 1854, $\nu$(NO) = 1589 cm$^{-1}$; $\delta$(W–*C*O): 257.3 (*t*, $^2J$(C,P) = 4.2 Hz) ppm) [6].




**7a**




**7b**

**Discussion.** – The reaction between the (pyridin-2-yl)-substituted aldehydes and ketones and **1** seems to proceed *via* a direct nucleophilic attack of the H-atom of **1** to the electrophilic C-atom of the C=O group (as evidenced by the formation of intermediates **2a** and **6a**) [7]. Thus, prior coordination of the substrate molecule to the W-centre, either through the O- or the N-atom, does not seem to occur. This is contrasted by the fact that the insertion reaction of **1** with the 6-Me-substituted pyridine-2-carbaldehyde is much slower than that with the non-substituted pyridine-2-carbaldehyde. Since, in the present view, we do not expect much steric repulsion between the pyridine moiety and the coordination sphere of W during the insertion process, there is no obvious reason why the rate of insertion should differ much. It is, however, possible that the actual insertion is preceded by a rate-determining electron-transfer step, as is seen for other insertion reactions, too [8]. In this respect, it is interesting to note the following observations. Thus, by IR or NMR, we do not observe any reaction between **1** and either pyridine, 4-(dimethylamino)pyridine, 2,2′-bipyridyl, or pyridine-4-carbonitrile. However, solutions of the latter two, rather electron deficient, pyridine derivatives develop reddish and purple colors, respectively (pure **1** has an orange color). In $CH_2Cl_2$ solution, this results in extra absorption bands in the UV/VIS area in addition to those already present for **1** and the corresponding pyridine derivative: $\lambda_{max} = 608$ nm with $\varepsilon = 100$ for 2,2′-dipyridyl, and $\lambda_{max} = 547$ nm with $\varepsilon = 370$ for pyridine-4-carbonitrile. This may be attributed to the formation of charge-transfer complexes, and although we do not know their exact structures, it is likely that there is not only an electronic but also a steric contribution to the stability of such associates. Thus, if one assumes electron transfer from the W-centre to the pyridine $\pi^*$ system to be the rate-determining step for the present insertion reactions, it becomes clear why the reaction of **1** with the sterically cumbersome but electronically similar 6-methylpyridine-2-carbaldehyde is so much slower than with pyridine-2-carbaldehyde.

Compared with the isosteric Ph group, the pyridin-2-yl group is a powerful activator for these insertion reactions [1]. The accelerating effect of the other keto substituent during these insertion reactions follows the order pyridin-2-yl > H > Ph > Me, and is consistent with the electron-withdrawing properties of these groups.

As mentioned before, the presence of a W–O (alkoxy) bond has a considerable labilizing effect on the adjacent CO ligands in the molecule (*cf.* in **2a** and **6a**). Consistent with this is the facile loss of CO that is observed with subsequent formation of *O,N*-coordinated alkoxy products. In fact, in most cases (except for **2** and **6**), the loss of CO seems to proceed at a faster rate than the insertion. The expected kinetic product from this CO loss, should have a structure with the alkoxy O-atoms *trans*-positioned to the NO ligand, and the pyridine *N*-atom *trans*-positioned to the CO ligand. In reality, however, it is the other CO/NO exchange isomer that is observed as the final product. Only for **6**, we observe the kinetic isomer **6b** as an unstable intermediate, isomerizing rapidly to its CO/NO exchanged congener **6c**. Apparently, loss of CO from **2a** and **6a** results in the formation of an intermediate in which the alkoxy moiety is able to flip rapidly between the adjacent *cis*-vacancy (*Scheme 2*)[6]). It also means that the *O,N*-bidentate-coordination mode in **6b**, and perhaps in **6c** too, must be reversible. It is our impression that bidentate

[6]) An alternative mechanism, that cannot be excluded, involves the intermediacy of a metallo-ester, formed by a reversible nucleophilic attack of the alkoxy moiety on an adjacent CO ligand.

anionic ligands in the $[W(CO)(NO)(PMe_3)_2]$ moiety that have quasi-aromatic character, like in salicyclates [1] or '$\beta$-diketonates' [9], are configurationally stable, and those that have not, like in the present case, are not. Obviously the *trans*-N–NO/*trans*-O–CO arrangement is thermodynamically more stable than its isomer, and we attribute this to the tendency of the NO ligand, having the strongest $\pi$-accepting properties of the four ligands, to line up *trans* to the ligand with the most powerful electron-donating properties, *i.e.* the pyridyl N-atom.

Finally, we notice the failure of reaction between **1** and imidazole-2-carboxaldehyde. Although, this substrate might also give rise to the formation a *O,N*-chelate-stabilized insertion product, the imidazole moiety apparently is a strongly deactivating group for the insertion.

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