

113. IR, Multinuclear-NMR, and Structural Studies on [WH(CO)₂(NO)(PR₃)₂]: *cis*-Influence of Phosphorus Ligands on Hydride Character

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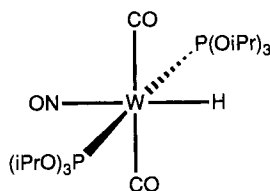
A thorough IR and ¹H-, ¹³C-, ³¹P-, ¹⁸³W-NMR spectroscopic, and X-ray structural study was carried out on complexes of the type *trans,trans*-[WH(CO)₂(NO)(PR₃)₂], (R = Et, Me, Ph, *i*-PrO, MeO, and PhO). Linear correlations could be found between Tolman's parameter *X* and $\nu(\text{CO})$, $\nu(\text{WH})$, $\nu(\text{NO})$, $\delta(^{13}\text{C})(\text{CO})$, as well as $\ln(k)$, *k* being the H/D exchange rate constant for the hydride in CD₃OD. The ¹*J*(¹⁸³W, ³¹P), ²*J*(³¹P, ¹H), and ²*J*(³¹P, ¹³C) as well as the ¹*J*(¹⁸³W, ¹H) values are related to the electronegativity of the R groups on the phosphorus ligands. This is also indicated by EHT calculations of s-orbital populations of appropriate W model complexes. The X-ray structures of [WH(CO)₂(NO)(PR₃)₂] (R = Me, Ph, and MeO) were determined. Minor differences were observed in the W–P bond lengths and in the P–W–P and C–W–C angles. No obvious relationship between X-ray data and spectroscopic parameters could be found. All three structures reveal a bending of both the CO and PR₃ ligands towards the hydride atom. The total octahedral distortion is remarkably constant (25.6, 29.4, and 27.0° tilt, respectively), although the ligands individually are very different. This is attributed to redistribution of π-electron density between CO and PR₃ groups toward the central W-atom in the three complexes.

Introduction. – The correlation of spectral and structural parameters of transition-metal complexes with the electronic and steric parameters of their ligands on the one hand, and with kinetic and thermodynamic parameters, *i.e.* reactivity, on the other hand is an important goal in chemistry. A quantization of the electronic and steric parameters of PR₃ ligands has been achieved by Tolman [2]. The cone angle θ has been introduced as a measure of the steric requirements, and the frequency of the A₁ CO mode in [Ni(CO)₃(PR₃)] is now a well-accepted measure (*X*) of the combined electronic σ-donor/π-acceptor properties of PR₃ ligands [3]. Recently, a quantitative separation of σ and π effects was made by correlating the former with the p*K*_a values of R₃PH⁺ [4]. Tolman's parameters have been linearly correlated mainly to C≡O stretching frequencies in other transition-metal complexes, but also to ¹³C-NMR chemical shifts of these carbonyls [5].

In our studies on the reactivity of nitrosyl metal hydrides, we recognized that the complex *trans,trans*-[WH(CO)₂(NO)[P(*i*-PrO)₃]₂] is remarkably basic, due to the presence of a W–H bond with highly hydridic character [6].

This was attributed to the *trans*-positioned NO ligand, which as a three-electron donor causes a general rise of the SOMO of the metal fragment and a concurrent polarisation of the metal–H bond [6] [7]. To study the *cis*-influence of the phosphorus ligands on the hydridic character, we set out a thorough spectroscopical and structural

¹⁾ Transition-Metal NMR Spectroscopy Part XX. Part XIX: [1].



investigation of complexes of the type *trans,trans*-[WH(CO)₂(NO)(PR₃)₂], using ligands which span a wide range in Tolman's electronic series (R = Et, Me, Ph, *i*-PrO, MeO, PhO). It was noticed that these compounds bear a number of NMR-active nuclei (¹H, ¹³C, ³¹P, and ¹⁸³W), which are all coupled to each other. Systematic changes of chemical shifts, coupling constants, and IR stretching frequencies were investigated, and attempts were made to relate them to electronic parameters of the PR₃ ligands and chemical reactivity. The X-ray structural investigation on three representatives of the series was carried out to study the influence of substituents on the molecular structure. An attempt was also made to relate X-ray to spectroscopic data.

Experimental. – IR: Biorad FTS-45. ¹H- and ¹³C-NMR: Varian Gemini-200. ³¹P-NMR: Varian XL-200. ¹⁸³W-NMR: Bruker AM-400-WB. MS: Finnigan MAT-8240; FAB-MS, solvent: THF; *m/z* in % relative to the highest peak based on ¹⁸⁴W.

¹⁸³W-Chemical shifts were determined by (¹H, ¹⁸³W)-HMQC correlation experiments. Generally the four-pulse sequence 90°(H)–1/(2·J(W,H))–90°(W)–*t*₁/2–180°(H)–*t*₁/2–90°(W)–acq(H) preceded by a BIRD_φ pulse-sandwich was used [8]. The phase φ was cycled in steps of 90°, and θ was alternatively set to 0° and 180° for consecutive cycles of φ. For 0.2M samples, typically 16 FID were accumulated for each of the 16 or 32 traces in *t*₁. The experiments took about 0.5 h and yielded spectra with good signal-to-noise ratio, but somewhat poor resolution in F1 due to fast relaxation of the heteronuclear double- and zero-quantum coherences (see Fig. 2).

All reactions and manipulations were carried out under an atmosphere of dry N₂ using freshly distilled solvents. [WH(CO)₂(NO)(PR₃)₂] with R = MeO, *i*-PrO, and PhO were synthesized according to Berke and Kundel [9], and with R = Ph according to Hillhouse and Haymore [10].

[WH(CO)₂(NO)(PEt₃)₂]. To a soln. of *cis,mer*-[W(CO)₃(NO)(PEt₃)₂][PF₆] (4.05 g, 6.0 mmol; prepared as described for the analogous phosphites [9]), and PEt₃ (1 ml) in 100 ml THF was added an excess of solid NaBH₄ (0.50 g, 13.2 mmol). This caused immediate evolution of CO. After refluxing the mixture for 10 min, the solvent was evaporated *in vacuo*. The by-product BH₃·PEt₃ was then sublimed out of the residue at 40–50° in high vacuum. The remaining darkbrown residue was then extracted with hexane (100 ml in total). Concentrating and chilling of the combined extracts afforded a reddish crystalline solid, melting below r.t. to a red oil. Yield: 2.0 g (65%). MS: 506 (50, [M–H]), 476/478 (ca. 90, [M–H], NO/CO), 448/450 (ca. 100, [M–H], CO, NO/CO), 420 (40, [M–H], 2 CO, NO).

[WH(CO)₂(NO)(PMe₃)₂]. [W(CO)₃(NO)(PMe₃)₂][PF₆] was prepared according to Honeychuck and Hersh [11]. The tungsten-hydride was prepared as for its PEt₃ analogue. Orange crystals. Yield: 70%. MS: 422 (100, [M–H]), 392/394 (40, [M–H], NO/CO), 364/366 (50, [M–H], CO, NO/CO). Anal. calc. for C 22.71, H 4.53, W 43.46; found: C 22.20, H 4.71, W 43.50.

H/D-Exchange Experiments. Tungsten hydride (0.10 mmol) was dissolved in 0.50 ml of CD₃OD. The decrease of the intensity of the hydride resonance was followed at regular intervals by ¹H-NMR at +22°. After the experiment, the solvent was evaporated *in vacuo*, and the IR spectrum of the residue was taken in hexane, revealing [WD(CO)₂(NO)(PR₃)₂] as the main product (some decomposition occurred for the PMe₃ derivative). Both Ph-containing tungsten hydrides were not measured because of their insolubility in CD₃OD.

X-Ray Analyses. Suitable crystals of [WH(CO)₂(NO)(PMe₃)₂] were grown by cooling a saturated soln. of the complex from 20 to –80° within 2 d; crystals of [WH(CO)₂(NO)(PPh₃)₂] were obtained by cooling a CH₂Cl₂ soln. of the complex to –80°, and crystals of [WH(CO)₂(NO)[P(OMe)₃]₂] were grown by slowly evaporating the solvent from a sat. hexane soln. at r.t. Each crystal was glued to the tip of a glass fiber and maintained in the cold N₂ stream of a Siemens P3 diffractometer. Cell constants and orientation matrix were obtained and refined from 20 to 40 centered reflections taken from a rotation photograph. Data were collected using the θ/2θ (PMe₃ derivative) or the Wycckoff scan technique (PPh₃ and P(OMe)₃ derivatives), using MoK_α radiation. Further relevant data on the

Table 1. Crystal Data for $[WH(CO)_2(NO)(PR_3)_2]$

R	Me	Ph ^{a)}	MeO
Formula	C ₈ H ₁₉ NO ₃ P ₂ W	C ₃₉ H ₃₃ Cl ₂ NO ₃ P ₂ W	C ₈ H ₁₉ NO ₉ W
Crystal size [mm ³]	0.3 × 0.3 × 0.4	0.4 × 0.2 × 0.1	0.3 × 0.4 × 0.7
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2/ <i>c</i>
<i>a</i> [Å]	13.167(2)	9.879(3)	9.840(3)
<i>b</i> [Å]	8.687(2)	10.930(3)	11.186(4)
<i>c</i> [Å]	13.569(2)	19.882(5)	8.345(4)
α [°]	90	74.85(2)	90
β [°]	98.17(1)	88.31(2)	110.71(3)
γ [°]	90	64.27(2)	90
<i>V</i> [Å ³]	1536.4(4)	1858.1(9)	859.1(6)
<i>Z</i>	4	2	2
<i>d</i> _c [g/cm ³]	1.829	1.573	2.006
Temp. [K]	233	243	236
2 θ Range [°]	2–52	4–55	4–57
No. reflections	3112	7389	2417
unique	2841	6892	2184
obs. [<i>F</i> > 6 σ (<i>F</i>)]	2246	6145	2052
<i>R</i> , <i>R</i> _w , values [%]	4.83, 4.75	4.60, 3.75	3.45, 4.14

^{a)} Contains four molecules of CH₂Cl₂ in the unit cell.

X-ray investigations are given in Table 1. The W-atom was located by direct methods; subsequent refinement and difference Fourier synthesis yielded the positions of all non-H atoms, which were refined anisotropically. The C-bonded H-atoms were put on idealized tetrahedral positions (C–H = 0.96 Å) with fixed temp. factors ($U_{iso} = 0.08 \text{ \AA}^2$, refined for the P(OMe)₃ compound) and allowed to ride on their carrier atoms. For the P(OMe)₃ derivative, the W-atom and the NO group were found to lie on a crystallographic two-fold axis, with each atom having a site occupancy factor of 0.5. Consequently, only one PR₃ ligand and one CO ligand were present in the asymmetric unit. The O-atoms of the P(OMe)₃ ligand were disordered and each refined over two different sites. For all three compounds, the metal-bound H-atom was fixed at 1.75 Å from the W-atom on the N–W axis. A semi-empirical absorption correction based on azimuthal scan data was applied. All calculations were performed on a Microvax 2000 computer using the SHELXTL PLUS system [12].

Results and Discussion. – *IR Measurements.* The IR data of *trans,trans*-[WH(CO)₂(NO)(PR₃)₂] (R = Et, Me, *i*-PrO, MeO, and PhO) in hexane solution are listed in Table 2. Due to insolubility, IR data for *trans,trans*-[WH(CO)₂(NO)(PPh₃)₂], recorded in a nujol medium, were taken from [10]. Electronic and steric parameters of the PR₃ ligands are also presented in Table 2. The CO, WH, and NO stretching frequencies are plotted against Tolman's parameter *X* in Fig. 1.

They all show a good positive linear correlation ($r = 0.991, 0.971, 0.979$, respectively). To our knowledge, this is the first time a linear correlation has been found between a metal–hydride stretching frequency and *X*. As an increase of *X* reflects an enhanced π -accepting capability of a phosphorus ligand [15], π -back bonding to the CO and NO ligands is reduced, and hence explains the observed increase of CO and NO stretching frequencies. On the other hand, σ -donation of the PR₃ ligands is decreased, which apparently strenghtens the W–H σ -bond. A similar effect may be seen in the isolobal octahedral d⁶ complexes *cis,trans*-[IrCl₂H(CO)(PR₃)₂] [16]; we notice that in those compounds, that have PR₃ ligands with cone angles up to *ca.* 150°, there is also a linear relationship of the Ir–H stretching frequency with *X*. Since the above explanation involves pure σ effects, it was anticipated that a better correlation might exist between the

Table 2. *Electronic and Steric Parameters of PR₃, IR Data and H/D exchange rates for [WH(CO)₂(NO)(PR₃)₂].*

R	$X^b)$	$\theta^c)$	$en_R^d)$	IR Data ^{a)}			$k^e)$
				$\nu(\text{CO})$	$\nu(\text{WH})$	$\nu(\text{NO})$	
Et	6.30	132	2.482	1912	1671	1592(1622)	4.1
Me	8.55,	118	2.472	1917	1665	1590(1627)	8.6
Ph	13.25	145	2.717	1921 ^{f)}	1681 ^{f)}	1596(1629) ^{f)}	g
i-PrO	19.05	130	3.544	1942	1702	1613(1637)	15
MeO	24.10	107	3.543	1952	1702	1619(1646)	77
PhO	30.20	128	3.525	1969	1721	1638	g

^{a)} Hexane solution with vs, s, s intensities. Values between parentheses are those from the corresponding tungsten *deuterides*.

^{b)} Tolman's parameter in cm^{-1} taken from [3].

^{c)} Cone angle of PR_3 ligand taken from [2].

^{d)} R-Group electronegativity taken from [13].

^{e)} Pseudo first-order H/D-exchange rate in $\text{CD}_3\text{OD} \times 10^5$.

^{f)} Data from [9], measured as a fluorolube mull.

^{g)} Insoluble in CD_3OD .

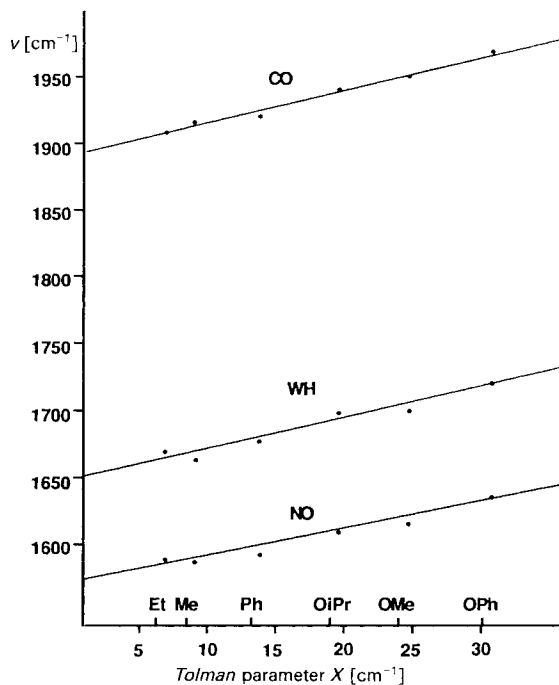


Fig. 1. CO, WH, and NO stretching frequencies of $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ vs. Tolman's parameter X

σ -donative component of X (X_s , quantified by *Giering* and coworkers [4]) and the W–H stretching frequency. This seems indeed the case, since the correlation coefficient improves from 0.971 to 0.996.

The W–H stretching frequencies for $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ are low (compare 1828 cm^{-1} for $[\text{WH}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$, 1912 for $[\text{WH}_2(\eta\text{-C}_5\text{H}_5)]$, and 1943 for $[\text{WH}_3(\eta\text{-C}_5\text{H}_5)_2]^+$ [17]), that for $[\text{WH}(\text{CO})_2(\text{NO})(\text{PMe}_3)_2]$ (1665 cm^{-1}) being one of the lowest ever reported for a non-bridged tungsten hydride. Subtracting a contribution from vibrational coupling with the *trans*-NO group (as is indicated by comparison of the $\nu(\text{NO})$ values of the tungsten hydrides and *deuterides* in Table 2), would lower these frequencies of these vibrations even more. The W–H bands have remarkably high intensities, as compared to those in most other metal hydrides [18], those of the PMe_3 and PET_3 complexes being even stronger than the NO bands. These observations reflect the low bond strength, as well as the polar, hydridic character of the W–H bond. It is concluded that the alkylphosphane derivatives $[\text{WH}(\text{CO})_2(\text{NO})(\text{PET}_3)_2]$ and $[\text{WH}(\text{CO})_2(\text{NO})(\text{PMe}_3)_2]$ have the most basic hydrides, whereas $[\text{WH}(\text{CO})_2(\text{NO})[\text{P}(\text{O}^i\text{Ph})_3]_2]$ has the most acidic one. This is expressed in its behavior towards protic reagents (*vide infra*).

NMR Measurements. Chemical Shifts. The ^1H -, ^{13}C -, ^{31}P -, and ^{183}W -NMR data of $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ complexes in C_6D_6 are given in Table 3. The ^1H hydride resonances show up as *multiplets* at relatively low field as compared to other metal hydrides. This seems to be a general feature for nitrosylmetal hydrides²⁾. Except for the PPh_3 complex, all the hydride resonances fall in a narrow range (–1.84 to –1.14 ppm). The strikingly deshielded value for the PPh_3 complex (+0.64 ppm) might be a result of anisotropic ring current effects of the adjacent Ph rings³⁾.

The ^{13}C resonances of the CO ligands in $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ show the expected [5] good linear correlation ($r = 0.989$) with *Tolman's* parameter X .

Table 3. NMR-Data for $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ ^{a)}

R	Chemical shifts ^{b)}				Coupling constants ^{c)}				
	W– ¹ H	W– ¹³ CO	W– ³¹ PR ₃ ^{d)}	¹⁸³ W	$J(^{183}\text{W}, ^1\text{H})$	$J(^{183}\text{W}, ^{31}\text{P})$	$J(^{13}\text{C}, ^1\text{H})$	$J(^{31}\text{P}, ^1\text{H})$	$J(^{31}\text{P}, ^{13}\text{C})$
Et	–1.84	220.0	8.6 (–20)	–2558	30.0	276	10.0	23.7	7.0
Me	–1.27	218.7	–32.7 (–64)	–2416	30.7	279	9.8	25.4	6.9
Ph	0.64	218.2	28.7 (–7)	–2279	31.4	288	10.5	22.4	6.4
i-PrO	–1.18	214.1	141.3 (137)	–2577	27.9	437	10.3	31.5	10.3
MeO	–1.59	211.2	151.9 (140)	–2686	26.7	444	10.2	33.0	10.2
PhO	–1.14	207.5	139.1 (128)	–2606	25.1	469	10.2	34.7	10.4

^{a)} C_6D_6 solution, at +24°.

^{b)} In ppm. $\delta(\text{H})$ relative to $\text{C}_6\text{D}_5\text{H}$ (7.15 ppm); $\delta(\text{C})$ relative to C_6D_6 (128.0 ppm); $\delta(\text{P})$ relative to external H_3PO_4 ; $\delta(\text{W})$ relative to external Na_2WO_4 , 1M in H_2O .

^{c)} In Hz. $^1J(^{183}\text{W}, ^1\text{H})$ and $^2J(^{31}\text{P}, ^1\text{H})$ were measured *via* ^1H -NMR, $^2J(^{13}\text{C}, ^1\text{H})$ and $^2J(^{31}\text{P}, ^{13}\text{C})$ *via* ^{13}C -NMR, and $^1J(^{183}\text{W}, ^{31}\text{P})$ *via* ^{31}P -NMR.

^{d)} Data in parentheses refer to the ^{31}P shifts of the free ligand which were taken from [20].

²⁾ We also observed low-field shifts of nitrosyliron and nitrosylrhenium hydrides [19].

³⁾ There is no anisotropic solvent effect involved in this, since in isotropic solvents like CDCl_3 or CD_3OD a general high-field shift of *ca.* 0.5 ppm for the hydride signals is observed, the value for the PPh_3 complex remaining exceptionally thereby.

The ^{31}P resonances for our complexes all show the usual downfield shift (Δ) as compared to the value of the free ligand. No obvious linear correlation was found between their absolute or relative values (Δ) and other spectral parameters, *Tolman's* parameter, PR_3 cone angle, or the electronegativity of the phosphorus substituents. It was, however, observed that the value of Δ of the phosphane complexes (*ca.* 30 ppm) was *ca.* 3 times as large as that of the phosphite complexes (*ca.* 10 ppm). This suggests a consistently smaller opening of the phosphite ligands upon complexation to W than for the phosphane ligands [2].

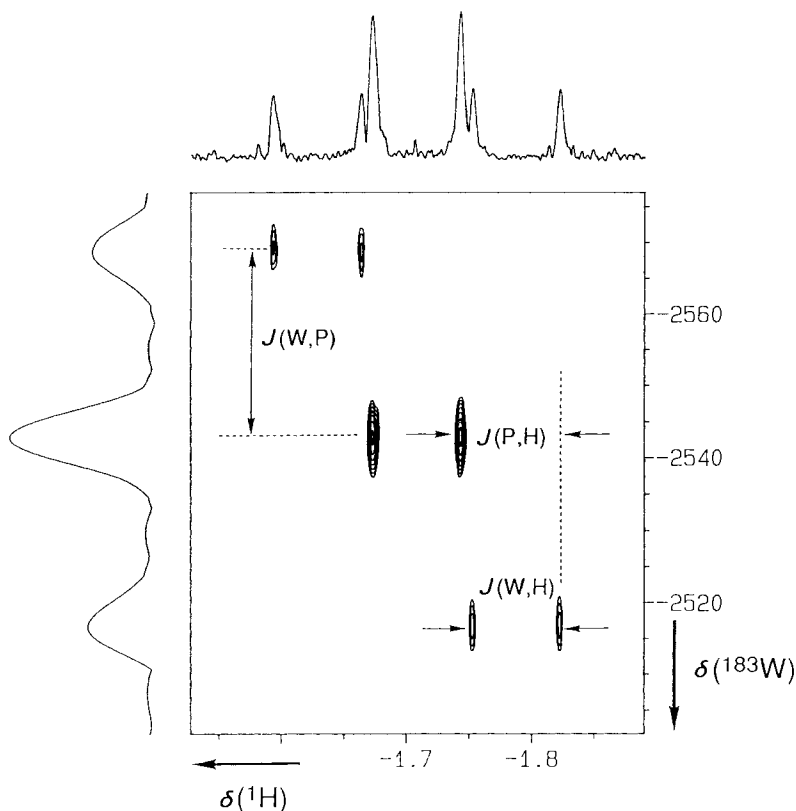


Fig. 2. (^1H , ^{183}W)-HMQC Spectrum of $[\text{WH}(\text{CO})_2(\text{NO})[\text{P}(\text{OiPr})_3]_2]$ in CDCl_3 at 300 K. The spectrum is shown in its magnitude representation. Apart from the ^{183}W chemical shift and the coupling constants, there is additional information to be noted: the tilt of the 2D multiplet indicates opposite signs of $^1J(^{183}\text{W}, ^{31}\text{P})$ and $^2J(^{31}\text{P}, ^1\text{H})$ which proved to be true for all our compounds. $^1J(^{183}\text{W}, ^{31}\text{P})$ is generally assumed to be positive [14].

The ^{183}W chemical shifts were measured by 2D (^1H , ^{183}W) correlation techniques, an example of which is depicted in Fig. 2.

The ^{183}W -nuclei in the phosphite complexes are more shielded than in the phosphane complexes. Attempts to quantify this effect, however, have been unsuccessful so far. *McFarlane* and coworkers observed a linear correlation of ^{183}W and ^{95}Mo shifts in complexes of the type $[\text{M}(\text{CO})_5(\text{PR}_3)]$ with various phosphorus ligands [21]. A linear relationship has also been found between ^{95}Mo chemical shifts in complexes of the type

[Mo(CO)₅(PR₃)] and *cis*-[Mo(CO)₄(PR₃)₂] [22]. We also find a fair correlation between the chemical shifts of ¹⁸³W in [WH(CO)₂(NO)(PR₃)₂] and, for instance, ⁹⁵Mo in [Mo(CO)₅(PR₃)] (*r* = 0.92). Therefore, it seems that there exists an electronic ranking of phosphorus ligands, different from that of *Tolman*, which systematically governs the chemical shifts of ⁹⁵Mo, ¹⁸³W, and maybe other nuclei in various complexes.

Coupling Constants. From *Table 3*, it is easily seen that coupling constants involving phosphorus, *i.e.* ¹*J*(¹⁸³W, ³¹P), ²*J*(³¹P, ¹H), and ²*J*(³¹P, ¹³C) are strongly dependent on the electronegativity (*en*_R, *Table 2*) of the substituents R of the PR₃ ligand. Other authors noticed a linear relationship between ¹*J*(¹⁸³W, ³¹P) and the electronegativity of the α-atom of PR₃ in [W(CO)₅(PR₃)] [23] or with p*K*_a of phosphanes [24]. We find a fair-to-good linear dependence of all three coupling constants with the R-group electronegativity, *i.e.* of ¹*J*(¹⁸³W, ³¹P) (*r* = 0.98), ²*J*(³¹P, ¹H) (*r* = 0.93), and ²*J*(³¹P, ¹³C) (*r* = 0.96).

R-Group electronegativity of the PR₃ ligands also seems to indirectly govern the magnitude of the ¹*J*(¹⁸³W, ¹H) coupling, although in a reverse way. Correlation with *en*_R is only fair (*r* = -0.88), but is better with the P-related coupling constants, *i.e.* with ¹*J*(¹⁸³W, ³¹P) (*r* = -0.94), ²*J*(³¹P, ¹H) (*r* = -0.97), and ²*J*(³¹P, ¹³C) (*r* = -0.93). One explanation for this phenomenon might be that more electronegative substituents on the P-atom concentrate more s-electron density in the W–P bond (increasing ¹*J*(¹⁸³W, ³¹P)), with a concomitant reduction in the W–H bond (decreasing ¹*J*(¹⁸³W, ¹H)). This, however, contradicts the IR data of [WH(CO)₂(NO)(PR₃)₂] which indicate stronger W–H bonds with increasing electronegativity of the R groups on P. Therefore, we conclude that in the present case the magnitude of the ¹*J*(¹⁸³W, ¹H) coupling is not a measure for the W–H bond strength.

The hydride-carbonyl coupling ²*J*(¹³C, ¹H) is remarkably constant throughout the six W complexes (*J* = 10.2 ± 0.4) and seems, therefore, not sensitive towards P-ligand substitution.

X-Ray Structures of [WH(CO)₂(NO)(PR₃)₂] (R = Me, Ph, and MeO). To study the structural effects resulting from changes of PR₃ ligands in *trans,trans*-[WH(CO)₂(NO)(PR₃)₂], single-crystal X-ray analyses were performed on three representatives of this series, namely [WH(CO)₂(NO)(PMe₃)₂], [WH(CO)₂(NO)(PPh₃)₂]·CH₂Cl₂, and [WH(CO)₂(NO)[P(OMe)]₂]. Selected bond lengths and angles are given in *Tables 4* and *5*, respectively. Their molecular structures are shown in *Fig. 3*.

It is noticed that the H-atoms could not be found during refinement, and accordingly were put on idealized positions. The molecules reside as discrete monomers in the crystal lattice. The central W-atom has a distorted octahedral coordination sphere, consisting of a linearly coordinated NO ligand, a presumably, perfectly *trans*-positioned H-atom and

Table 4. Selected Bond Lengths [Å] in [WH(CO)₂(NO)(PR₃)₂]

R	Me	Ph	MeO	R	Me	Ph	MeO
W–P(1)	2.469(3)	2.501(2)	2.432(2)	[P–X] _{av} ^a	1.81(3)	1.833(9)	1.60(5)
W–P(2)	2.457(4)	2.489(2)		N–O(1)	1.200(15)	1.196(6)	1.174(13)
W–N	1.834(10)	1.842(5)	1.846(9)	C(1)–O(2)	1.174(19)	1.138(10)	1.143(11)
W–C(1)	2.011(16)	2.033(8)	2.021(8)	C(2)–O(3)	1.170(18)	1.141(8)	
W–C(2)	2.048(14)	2.038(6)					

^a) X = C for R = Me and Ph; X = O for R = MeO.

Table 5. Selected Bond Angles [°] in $[WH(CO)_2(NO)(PR_3)_2]$

R	Me	Ph	MeO ^{a)}	R	Me	Ph	MeO ^{a)}
P(1)–W–P(2)	164.4(1)	170.9(1)	167.6(1)	N–W–C(2)	94.5(5)	100.2(2)	
P(1)–W–N	97.7(3)	94.6(2)	96.2(1)	C(1)–W–C(2)	170.0(6)	159.7(2)	165.4(4)
P(2)–W–N	97.9(3)	94.5(2)		W–N–O(1)	178.9(10)	178.8(6)	180.0(1)
P(1)–W–C(1)	86.9(5)	90.0(2)	90.3(2)	W–C(1)–O(2)	178.3(12)	176.9(5)	176.0(6)
P(2)–W–C(1)	92.2(4)	89.4(2)		W–C(2)–O(3)	177.1(12)	176.7(6)	
P(1)–W–C(2)	89.8(4)	89.9(2)	88.1(2)	[W–P–X] _{av} ^{b)}	116(2)	115(2)	117(3)
P(2)–W–C(2)	88.4(4)	87.5(2)		[X–P–X] _{av} ^{b)}	102(2)	103(3)	10(5)
N–W–C(1)	95.3(5)	100.0(2)	97.3(2)				

^{a)} Because of the presence of a C_2 axis in the MeO derivative, P(2), C(2), and O(3) correspond to symmetry-rotated P(1), C(1), and O(2) atoms.

^{b)} X = C for R = Me and Ph; X = O for R = MeO.

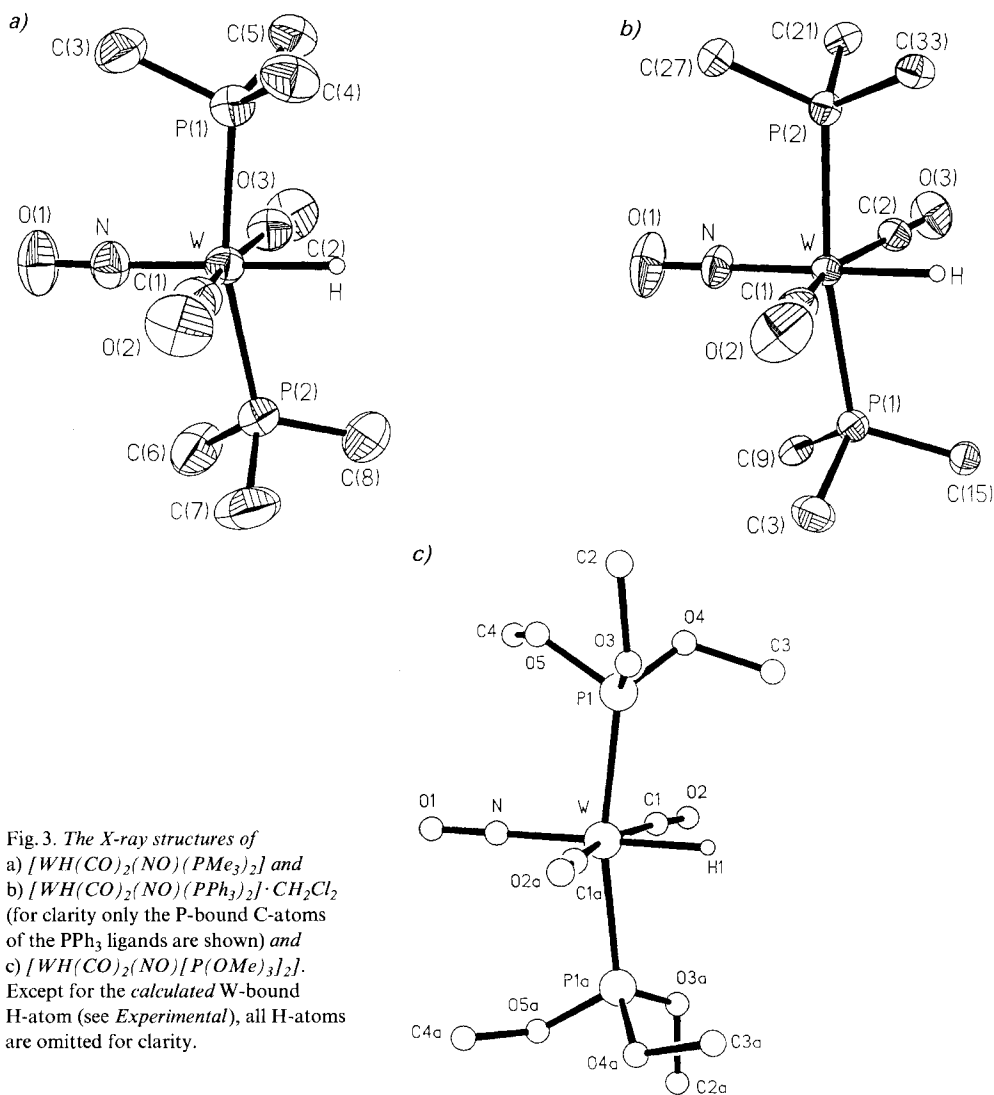


Fig. 3. The X-ray structures of
 a) $[WH(CO)_2(NO)(PMe_3)_2]$ and
 b) $[WH(CO)_2(NO)(PPh_3)_2] \cdot CH_2Cl_2$
 (for clarity only the P-bound C-atoms
 of the PPh_3 ligands are shown) and
 c) $[WH(CO)_2(NO)[P(OMe)_3]_2]$.
 Except for the calculated W-bound
 H-atom (see Experimental), all H-atoms
 are omitted for clarity.

two sets of *cis*-, mutually *trans*-positioned, CO and PR₃ ligands. The four CO and PR₃ ligands are slightly bent towards the H-atom, as is expressed by the < P–W–P angles (164.4(1), 170.9(1), and 167.6(1)°) and the < C–W–C angles (170.0(6), 159.7(2), and 165.4(4)°, respectively for the Me, Ph, and MeO derivative). Although the individual bending of either the PR₃ and CO ligands is quite irregular, the total angular octahedral distortion is remarkably constant in the three complexes (25.6, 29.4, and 27.0°). The NO group, being a powerful π acceptor, weakens π -back bonding to all *cis*-positioned ligands through either the d_{xz} or d_{yz} orbitals (*z* is along the ON–W–H axis), which then results in bending of these ligands towards the σ -bonded H-atom. The total amount of bending, being independent of the kind of PR₃ ligand, results from a competition between the CO and PR₃ ligands for π -electron density in the *xy*-plane. The outcome of this competition will depend on both electronic and steric factors and possibly also on crystal packing effects.

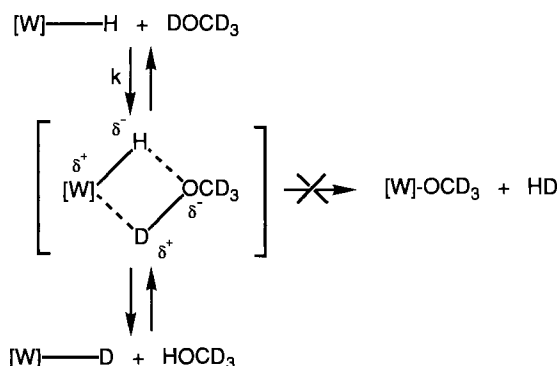
Another significant difference between the three crystal structures is found in the W–P distance, being 2.463(4)_{av}, 2.495(2)_{av}, and 2.432(2) Å for the Me, Ph, and MeO derivative, respectively. We were not able to correlate these bond lengths with any other spectroscopic parameter of the respective compounds. A linear correlation between M–P bond length and PR₃ ligand cone angle has been demonstrated in some cases [4].

Within the limited accuracy of the X-ray data, it may be seen that the trend in $\nu(\text{NO})$ and $\nu(\text{CO})$ IR data is reflected in the respective NO and CO bond lengths, *i.e.* a smaller stretching frequency is associated with a shorter bond length.

EHT Calculations. EHT Calculations [25] on a [WH(CO)₂(NO)(PH₃)₂] model molecule indicate that the *s*-orbital population on W is reduced from 0.117 to 0.091, if the P *Coulomb* energy is lowered by 4 eV. At the same time, we find a reverse correlation for the *s*-orbital population on the P center, which increases from 0.835 to 1.0. Both trends would be in agreement with those observed for the NMR coupling parameters $^1J(^{183}\text{W}, ^1\text{H})$ and $^1J(^{183}\text{W}, ^{31}\text{P})$. Since, however, the *s*-orbital population does not mirror the total bond order of the transition-metal ligand interactions, which would include *p*- and especially *d*-orbital occupancies, it is obviously not possible to mimic bond strength or $\nu(\text{W–H})$ IR frequencies by NMR parameters. A deviation of the CO and PR₃ ligands from equatorial plane bending toward the H-atom would also cause a decrease of the W *s*-orbital population and in addition of the total W–H bond population. But, since the differences in these bending effects are rather small, as demonstrated by the X-ray structure determinations of [WH(CO)₂(NO)(PR₃)₂] (R = Me, Ph, MeO), the electronic influence originating from such equatorial distortions should be negligible under realistic chemical conditions.

H/D-Exchange Experiments. The acidity/basicity of [WH(CO)₂(NO)(PR₃)₂] was examined by H/D exchange of our complexes in CD₃OD. Except for the two Ph-containing compounds, all were found to be soluble in this medium. Moreover, no elimination of dihydrogen and formation of [W(OCD₃)(CO)₂(NO)(PR₃)₂] was observed during the experiments (some decomposition, however, was observed for the PMe₃ derivative). Exchange rates (*k* see Table 3) were found to follow pseudo first-order behavior with halflives of the tungsten hydrides ranging from 12 min (R = MeO) to 5 h (R = Et). The value of ln *k* was found to be linearly correlated to *Tolman*'s parameter (*r* = 0.94). The mechanism which has been put forward for such an H/D exchange is depicted in the Scheme [26].

Scheme



The proposed intermediate will be more stable, if the strongly polarized O–D bond in CD_3OD encounters a polarized W–H bond which is not too hydridic. Therefore, the more acidic tungsten hydrides (bearing phosphite ligands) will react faster with CD_3OD than the more basic ones.

The IR spectra of $[WD(CO)_2(NO)(PR_3)_2]$ obtained after the H/D-exchange experiment are listed in *Table 3*. Within 1 cm^{-1} , the CO stretching frequencies were unchanged. The W–D stretching frequencies, expected at *ca.* 1200 cm^{-1} , could not be located unambiguously. The NO frequency, being strongly coupled to the *trans*-positioned W–H/D bond is shifted to higher energy, thereby maintaining its correlation with *Tolman's* parameter ($r = 0.984$).

Conclusions. – We have demonstrated that in complexes of the type $[WH(CO)_2(NO)(PR_3)_2]$, the hydridic character of the W–H bond, as expressed in its reaction with CD_3OD , can be directly correlated with *Tolman's* electronic parameter, which in turn can be linearly correlated with the WH, CO, and NO stretching frequencies as well as with the ^{13}C -NMR chemical shifts of the CO groups of the compounds. The 1H chemical shift of the hydride atom, as well as the magnitude of the $^1J(^{183}W, ^1H)$ coupling, do not seem to be a good probe for the W–H bond strength or polarity. As supported by EHT calculations on s-population densities, NMR coupling constants in the present complexes seem to be mainly influenced by the electronegativity of the R groups in PR_3 .

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