Reactivity of [1,2-Bis(dimethylphosphanyl)ethane](mesitylidyne)tungsten(IV) Hydride with Group 7 and 8 Transition Metal Carbonyl Complexes

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Keywords: Hydride complexes / Formyl complexes / Decarbonylation

The reaction between the tungsten hydride complex *trans*-W(CMes)(dmpe)$_2$H [**1**, dmpe = 1,2-bis(dimethylphosphanylethane)] and a series of electrophilic transition metal carbonyl compounds has been investigated, to explore the generality of W–H reductions of coordinated CO. Hydride transfer to the mononuclear [Fe(CO)$_5$], and to the dinuclear [Re$_2$(CO)$_{10}$], yields the neutral heterobimetallic formyl complexes *trans*-W{(μ-OCH)Fe(CO)$_4$}(CMes)(dmpe)$_2$ (**2**) and *trans*-W{(μ-OCH)Re$_2$(CO)$_9$}(CMes)(dmpe)$_2$ (**3a**), respectively. In the latter case, after one week at room temperature, **3a** is smoothly converted into the stable ionic complex [W(CMes)(CO)(dmpe)$_2$]$^+$[Re$_2$(CO)$_9$H]$^-$ (**3b**). Reaction with the cluster [Ru$_3$(CO)$_{12}$] results in the formation of an unstable formyl complex, which undergoes a direct rearrangement at –20 °C to produce the ionic complex [W(CMes)(CO)(dmpe)$_2$]$^+$-[Ru$_3$(CO)$_{11}$H]$^-$ (**4**) as the final product. The molecular structure of **4** was unambiguously established by single-crystal X-ray diffraction.

Introduction

In recent years our group has investigated the chemistry of activated transition metal hydrides. It has been shown that the carbyne ligand plays a prominent role in the electronic activation of hydride units.[1,2]

The reactivity of **1** towards small unsaturated organic molecules has been studied.[2] These studies, together with density functional calculations,[3] have indicated an enhanced hydricity and a weakness of the W−H bond, due mainly to the mesityl carbyne ligand in the *trans* position, which is known to exert a strong *trans* influence/effect.[4] The use of dmpe ligands, which are strong σ-donors and less effective π-acceptors than (for example) CO, should lead to increased electron density on the metal, and also to enhanced stability of the corresponding metal formyl moieties. Until 1973, when the first isolated anionic formyl complex [(CO)$_4$Fe(CHO)]$^-$ was reported by Collman and Winter,[5] these compounds were conspicuous by their absence from the chemical literature. The first neutral formyl complex, Os(Cl)(CO)$_2$(PPh$_3$)$_2$(CHO), was reported by Collins and Roper in 1976.[6] In the same year, Casey, Gladysz, and Winter[7] reported the first anionic formyl complexes, formed by treatment of suitable hydride sources (in most cases, main group metal "super hydrides") with metal carbonyls. Nelson,[8] however, demonstrated that a transition metal hydride can also be effective as the hydride source. The vast majority of known metal formyl complexes are, however, thermally unstable with respect to decarbonylation.[9] Notable exceptions are the early transition metal complexes,[10] the rhodium porphyrin hydride complex RhOEP(H) (OEP = octaethylporphyrin) described by Wayland and co-workers,[11] and some actinohydrides[12] which produce η^2-formyl products. Transition metal formyl complexes and hydridometal carbonyls are commonly invoked as reactive intermediates in both catalytic and stoichiometric CO reduction reactions.[13] The synthesis and characterization of formyl-metal complexes remains important for fuller investigation of the mechanism of Fischer−Tropsch[14a] reductive hydrogenation of carbon monoxide to hydrocarbons and oxygenates proposed by Olivé and Olivé,[14b] in which the insertion of carbon monoxide into a metal−hydrogen bond to produce a formyl complex is considered to be the initial step. Coordinated CO can be inserted into the M−H bond of metal hydrides,[15] particularly when the reaction is driven by the oxophilic character of early transition metals, allowing formation of η^2-formyl complexes. The generation of η^1-formyl species is generally thermodynamically unfavourable, as demonstrated by several quantum chemical calculations.[16] We therefore examined the reaction between **1** and CO bound in metal carbonyl compounds, in order to explore the generality of W−H addition across the CO bond.

Results and Discussion

Treatment of **1** with one equivalent of [Fe(CO)$_5$] (at room temperature in THF for a few minutes) did indeed quantitatively produce the dinuclear formyl-bridged complex *trans*-W{(μ-OCH)Fe(CO)$_4$}(CMes)(dmpe)$_2$ (**2**, Scheme 1). The mechanism is presumed to involve H$^-$ transfer to a CO ligand, by direct nucleophilic attack on a metal-bound CO. Dedieu and Nakamura have carried out extensive ab initio SCF calculations on the hypothetical gas phase reaction between H$^-$ and [Fe(CO)$_5$], and have concluded that for the [(CO)$_4$FeCHO]$^-$ ion, direct H$^-$ addition to an axial CO is strongly exothermic and occurs without activation.[17] Casey and Neumann have reported a variety of metal formyl compounds, including [Fe(CO)$_4$CHO]$^-$, resulting from the reaction between [Na$^+$][HB(OR)$_3^-$] and M(CO)$_x$.[20]

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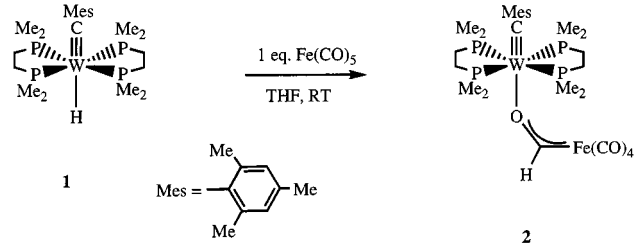
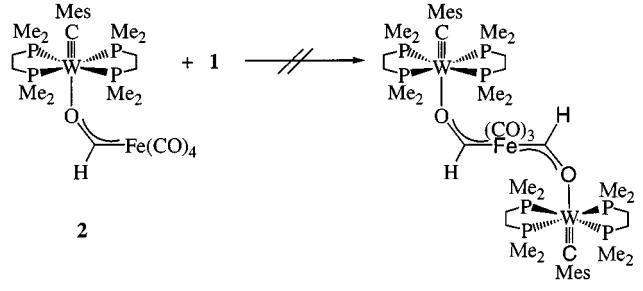


Scheme 1

Compound **2** was isolated, in 84% yield, as an orange, microcrystalline powder after recrystallisation from a saturated diethyl ether solution.

Among other resonances, the ^{1}H NMR spectrum of **2** features a characteristic H_{formyl} nucleus signal at $\delta = 13.67$, in the region reported for $K^+[Fe(CO)_4CHO]^-$ ($\delta = 15.0$)[7d] and *mer*-Mo{(μ-OCH)Fe(CO)$_4$}(CO)(NO)(PMe$_3$)$_3$ ($\delta = 14.09$).[19a] The ^{31}P{^{1}H} NMR spectrum features a singlet at $\delta = 32.2$ for the four equivalent phosphorus nuclei, with satellites from coupling to ^{183}W ($^1J_{PW} = 288$ Hz). The ^{13}C{^{1}H} NMR spectrum includes a quintet at $\delta = 298.6$ for the C_{formyl} atom ($^3J_{CP} = 5$ Hz), shifted by 39 ppm to lower field as compared to $[Fe(CO)_4CHO]^-$,[7b] and another quintet at $\delta = 275.3$ ($^2J_{CP} = 10$ Hz) for the carbyne carbon atom. These chemical shift values can be attributed to more efficient electron withdrawal in the bridging coordination mode. Evidence for the presence of a formyl ligand is most easily found in the IR spectral data. The THF solution infrared spectrum of **2** shows three bands at 2045 (m), 1967 (m) and 1932 (s) cm^{-1} − attributable to the terminal ν(CO) vibrations of the Fe(CO)$_4$ unit − and one other band at 1576 (m) for the iron formyl. This absorption pattern closely resembles that of the reported anion $[Fe(CO)_4CHO]^-$ complex.[18] Compound **2** provided an elemental analysis consistent with the proposed formula.

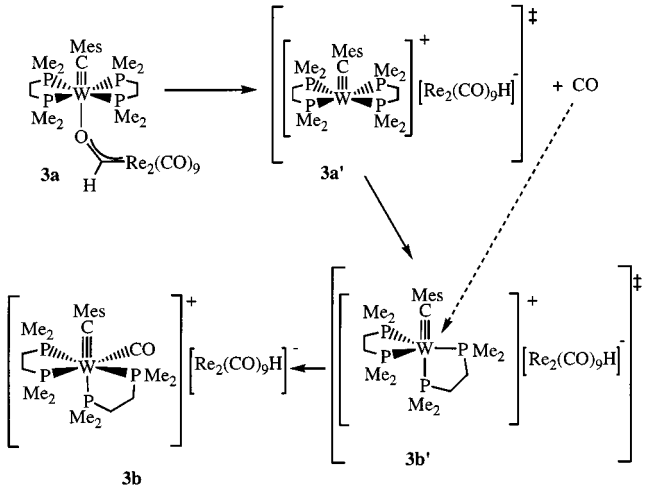
It was also expected that **2** would react further with excess **1**. Reaction with up to 10 equivalents of **1** at room temperature was therefore attempted, but no further transformations could be observed, indicating that the remaining carbonyls are inert towards further reduction to (for example) a bis(formyl) complex (Scheme 2).



Scheme 2

Steric hindrance probably makes the remaining CO ligands less susceptible to hydridic attack. On heating the reaction mixture at 60 °C for two days, the expected hydride migration to the iron was not detected, and neither was CO ejection. Compound **2** seems to be unusually stable; in the solid state it can be stored at room temperature under inert atmosphere for several weeks without any deterioration.

The reaction between **1** and one equivalent of $[Re_2(CO)_{10}]$ in THF was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and the primary insertion product (i.e., the formyl-bridged compound *trans*-W{(μ-OCH)Re$_2$(CO)$_9$}(CMes)(dmpe)$_2$ (**3a**)) was detectable almost immediately (Scheme 3).



Scheme 3

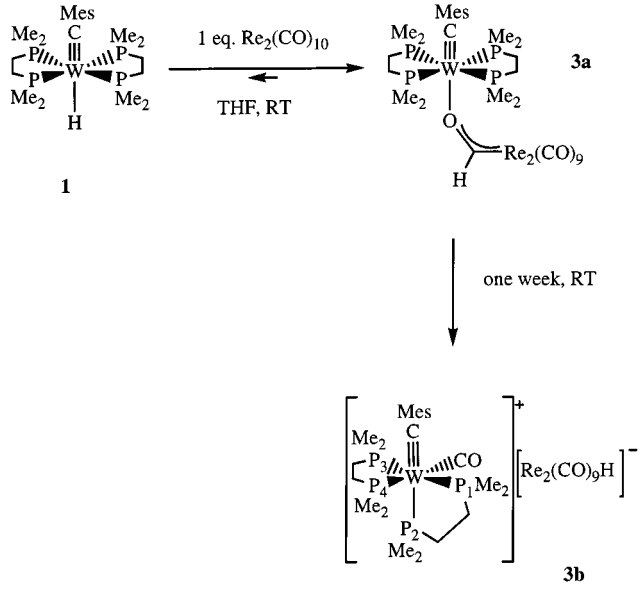
This reaction proceeds smoothly at room temperature, resulting in the formation of a clear orange/red solution. Here, again, the bridging formyl group of **3a** gives rise to characteristic NMR resonances. The ^{1}H NMR spectrum shows the H_{formyl} resonance at $\delta = 14.98$, close to those observed in $Li^+[Re_2(CO)_9(CHO)]^-$ [15,26] and *mer*-Mo{(μ-OCH)Re$_2$(CO)$_9$}(CO)(NO)(PMe$_3$)$_3$ ($\delta = 15.07$).[19a] ^{31}P{^{1}H} NMR spectroscopy reveals a singlet at $\delta = 29.9$ for the four equivalent phosphorus nuclei, with satellites from coupling to ^{183}W ($^1J_{PW} = 287$ Hz). The ^{13}C{^{1}H} NMR spectrum features a resonance at $\delta = 295.1$ for Re*C*HO. During the course of the reaction, the THF solution infrared spectrum had shown the ReCHO ν(C=O) band at 1535 cm^{-1}. However, unlike the reaction with [Fe(CO)$_5$], an equilibrium − lying to the right hand side, in favour of the product (ratio of **1**/**3a**, 2:3) − seems to have been reached after two days. This was also observed in the case of the similar compound *mer*-Mo{(μ-OCH)Re$_2$(CO)$_9$}(CO)(NO)(PMe$_3$)$_3$.[19a] At the same time, the emergence of a series of large multiplets in the dmpe region of the ^{1}H NMR spectrum was observed. The ^{31}P{^{1}H} NMR spectrum also displayed a number of new resonances. These signals are attributable to the isomeric ionic compound $[W(CMes)(CO)(dmpe)_2]^+[Re_2(CO)_9H]^-$ (**3b**). The colour of the solution mixture was brown at this point, and after one week at room temperature, almost 95% yield of this new salt material **3b** was observed spectroscopically (^{31}P{^{1}H} NMR). The ^{31}P{^{1}H} NMR spectrum features four multiplets of intensity 1:1:1:1 for the four chemically different phosphorus atoms at $\delta = 16.8$ (ddd, $^2J_{P3,P4} = 5$ Hz, $^2J_{P3,P2} = 21$ Hz, $^2J_{P3,P1} = 63$ Hz, $^1J_{P3,W} = 249$ Hz, P3), 14.4 (dd, $^2J_{P1,P3} = 65$ Hz, $^2J_{P1,P4} = 20$ Hz, $^1J_{P1,W} = 294$ Hz,

P1), 8.2 (ddd, $^2J_{P4,P1}$ = 20 Hz, $^2J_{P4,P2}$ = 25 Hz, $^2J_{P4,P3}$ = 5 Hz, $^1J_{P4,W}$ = 202 Hz, P4) and −15.5 (dd, $^2J_{P2,P3}$ = 21 Hz, $^2J_{P2,P4}$ = 23 Hz, $^1J_{P2,W}$ = 35 Hz, P2). The chemically distinct phosphorus atoms P1, P2, P3, and P4 have been assigned as described in Scheme 3. The assignments are in agreement with previously published data[4] and reflect the *trans* influence of the carbyne group on P2. It is therefore weakly bonded to the tungsten centre with a small coupling constant ($^1J_{P,W}$ = 35 Hz). For the same reason, $^2J_{P2,P1}$ is apparently so small as to be undetectable. The ^{1}H NMR spectrum shows a singlet at δ = −17.47 for the Re−H hydride and a series of multiplets in the dmpe region, due to the new arrangement of the dmpe ligands around the tungsten centre. The ^{13}C{^{1}H} NMR spectrum displays a multiplet at δ = 293.7 for the mesitylidyne carbon, due to the coupling with the four different phosphorus atoms, and another multiplet at δ = 230 for the W−CO carbon atom ($^2J_{C,P4}$ = 11 Hz). The THF solution infrared spectrum displays, among other characteristic resonances, one band at 1915 cm^{-1} (s), consistent with a terminal W−CO bond. After isolation, **3b** also gave satisfactory elemental microanalytical data.

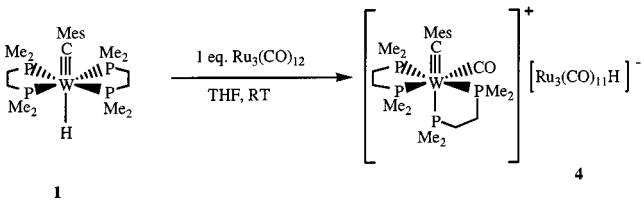
An intrinsic chemical property of transition metal formyl complexes is the capability to transfer a hydride ion to several classes of substrate (such as ketones, alkyl halides, or metal carbonyls), thereby acting as hydride donors. The lability of this metal formyl hydrogen was unambiguously demonstrated with isolated formyl complexes about twenty years ago.[7a,20,21] We propose, after initial attack by H$^-$ directly on coordinated CO, an intramolecular hydride migration from the formyl to the Re, presumably with initial loss of CO − i.e., a slow decarbonylation of **3a** at room temperature − to give the unsaturated complex **3a′**, with subsequent rearrangement around the tungsten centre to give **3b** (Scheme 4). The assumed five-coordinate, square-pyramidal cationic intermediate **3a′** is fluxional by the Berry mechanism (pseudorotation) and gives rise to the trigonal-bipyramidal **3b′** intermediate, which is then trapped by the free CO ligand to give **3b**. It is interesting at this stage to note that a CO ligand in a position *trans* to a carbyne unit has never been observed.[22] The rate-determining step in this reaction seems to be the decarbonylation step.

For *mer*-M(H)(CO)(NO)(PMe$_3$)$_3$ (M = Mo, W), it has been calculated that interaction with transition metal carbonyls such as [Fe(CO)$_5$] and [Re$_2$(CO)$_{10}$] is determined by secondary effects such as solvation or steric interactions, since both carbonyl complexes possess comparable hydride affinities.[19a][19b] For the related carbyne complexes, it is anticipated that similar selectivities with a similar physical background apply.

Compound **1** reacts with one equivalent of the triruthenium cluster [Ru$_3$(CO)$_{12}$] under ambient laboratory conditions in THF to afford the compound [W(CMes)(CO)(dmpe)$_2$]$^+$[Ru$_3$(CO)$_{11}$H]$^-$ (**4**) (Scheme 5), presumably formed via a formyl intermediate. In fact, when the reductive reaction is monitored at −50 °C in [D$_8$]THF, the ^{1}H NMR spectrum displays a resonance at δ = 15.6, suggesting that a pendant formyl moiety has been produced. However, upon raising the temperature in the NMR tube to −20 °C, the formyl signal gradually decreases, with concomitant appearance of a new band (s, Ru−H) at δ −12.05, assigned to **4**. It is known that most of the formyl intermediates are likely to decompose more rapidly than they form.[23] These decomposition reactions of formyl complexes, into the corresponding metal hydride with loss of CO, have received a great deal of attention,[9,24] and radical processes have been invoked in many cases. It is still not clear, however, whether this decomposition is determined by thermodynamic factors or is kinetic in origin.[25] The balance between these will depend on the mechanism of CO loss. For the anticipated cluster formyl complex *trans*-W{(μ-OCH)Ru$_3$(CO)$_{11}$}(CMes)(dmpe)$_2$, the decarbonylation step seems to be facilitated relative to that of **3a**. The fact that the stability of cluster formyl complexes is lower than that of the related mononuclear species has already been noted by Thornback et al.[26] These workers suggested that this instability is associated with the availability of an "α-elimination" mechanism in cluster systems, related to the β-elimination observed in mononuclear systems.



Scheme 4



Scheme 5

The reaction proceeds smoothly at room temperature in THF and is complete within a few minutes. Compound **4** can be isolated in 82% yield as a brown, microcrystalline powder after recrystallisation from a saturated diethyl ether solution. The ^{1}H NMR spectrum features a characteristic singlet at δ = −12.05 for the Ru−H hydride moiety in the cluster anion [HRu$_3$(CO)$_{11}$]$^-$,[27] which is consistent with

the value reported in the literature ($\delta = -12.9$).[28] The $^{31}P\{^1H\}$ NMR spectrum shows four different multiplet signals of intensity 1:1:1:1 at $\delta = 15.9$ (ddd, $^2J_{P3,P1} = 66$ Hz, $^2J_{P3,P2} = 20$ Hz, $^2J_{P3,P4} = 6$ Hz, $^1J_{P3,W} = 269$ Hz, P3), 13.9 (dd, $^2J_{P1,P3} = 65$ Hz, $^2J_{P1,P4} = 19$ Hz, $^1J_{P1,W} = 283$ Hz, P1), 7.8 (ddd, $^2J_{P4,P1} = 19$ Hz, $^2J_{P4,P2} = 25$ Hz, $^2J_{P4,P3} = 6$ Hz, $^1J_{P4,W} = 223$ Hz, P4), and -15.6 (dd, $^2J_{P2,P3} = 20$ Hz, $^2J_{P2,P4} = 25$ Hz, $^1J_{P2,W} = 20$ Hz, P2) for the four nonequivalent phosphorus nuclei. The different phosphorus atoms P1, P2, P3, and P4 have been assigned as described on Figure 1. Atom P2 is again, as in **3b**, very weakly bound with the tungsten centre, and therefore the $^1J_{PW}$ is very small: $^1J_{P2,W} = 20$ Hz. This is not surprising, given the assumed strong *trans* influence/effect of the carbyne ligand in the *trans* position. Consequently, the value of the coupling constant $J_{P2,P1}$ is also very small and has been calculated to be around 2 Hz (Table 1). This is also confirmed by the X-ray structure (Figure 2), in which the long W−P2 distance [2.664(4) Å], compared to the other W−P bond lengths, which are around 2.45, can be seen. Here, as for **3b**, the $^{13}C\{^1H\}$ NMR spectrum once more shows a multiplet at $\delta = 292$, which corresponds to the $C_{carbyne}$ carbon; this value is also further downfield than expected (shifted by 31.6 ppm relative to **1**), presumably due to the weakly bound phosphorus atom in the *trans* position. The infrared spectrum in THF solution exhibits, among other characteristic bands, one band at 1900 cm^{-1} (s) for the W-CO terminal carbonyl group. Compound **4** also gave a satisfactory elemental microanalysis. The $^{31}P\{^1H\}$ NMR spectrum of **4** (Figure 1) has been simulated and calculations carried out in order to evaluate the coupling constants between the four different phosphorus nuclei (Table 1).

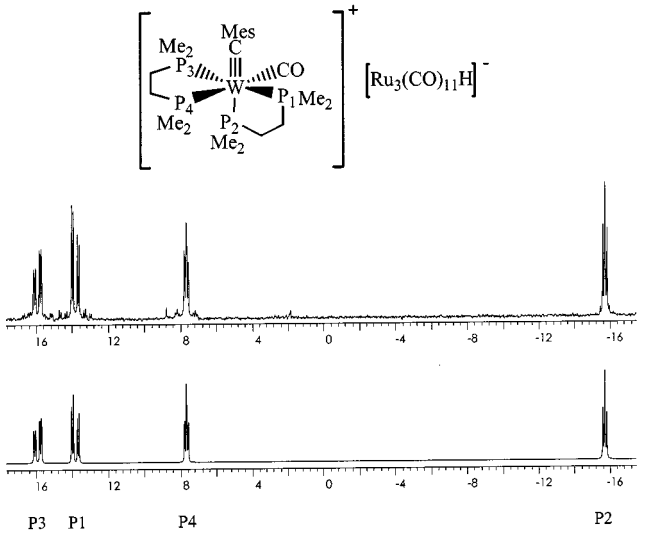


Figure 1. Measured (upper) and simulated (lower) spectra for the dmpe ligands in the $^{31}P\{^1H\}$ NMR spectrum of **4**

Table 1. Calculated shifts and coupling constants between P1, P2, P3, and P4 in compound **4**

Nucleus	Shift (ppm)	Width (Hz)	*J*, P1 (Hz)	*J*, P3 (Hz)	*J*, P4 (Hz)
P1	13.9	4.3		64.6	
P2	−15.7	5.5	2	20.8	23.5
P3	15.9	4.1			
P4	7.7	3.7	19.5	5.8	

Molecular Structure of 4

The structure of the separated ionic complex $[W(CMes)(CO)(dmpe)_2]^+[Ru_3(CO)_{11}H]^-$ (**4**) was finally established unequivocally by single-crystal X-ray diffraction (Figure 2 and Table 2). Suitable crystals were obtained by slow cooling of a saturated diethyl ether solution to −30 °C. Unfortunately, the X-ray structure analysis of **4** was hampered by the poor quality of the crystals, and attempts to achieve suitable crystals of **2** and **3b** were unsuccessful. Therefore, large standard deviations were found for the bond lengths and angles. Selected bond lengths (Å) and angles (°) are listed in Table 3.

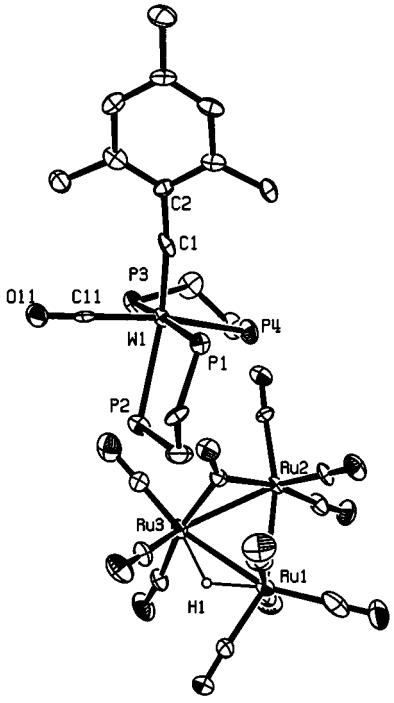


Figure 2. ORTEP plot of compound **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogens (except H1) and the Me carbon atoms from the dmpe ligands are omitted for clarity

Compound **4** adopts a pseudo-octahedral geometry, with the carbyne and one phosphorus in axial positions and the equator defined by 3 phosphorus atoms and the carbonyl group.

Conclusions

The results discussed above show that the tungsten hydride complex *trans*-$W(CMes)(dmpe)_2H$ **1** readily reduces group 7 and 8 transition metal carbonyls, acting as a hydride-based nucleophile towards metal-bound CO.

Table 2. X-ray crystal structure, data collection and refinement data for **4**

empirical formula	$C_{34}H_{44}O_{12}P_4Ru_3W$
fw	1255.63
temperature [K]	183(2)
wavelength [Å]	0.71073
cryst habit	dark red block single crystal
cryst size	0.18×0.17×0.14
cryst syst	triclinic
space group	$P\bar{1}$
a [Å]	13.617(1)
b [Å]	13.6388(9)
c [Å]	14.8427(9)
α [deg]	101.211(8)
β [deg]	99.319(8)
γ [deg]	117.923(7)
volume [Å^3]	2285.1(3)
Z	2
density (calcd) [Mg/m^{-3}]	1.825
abs coeff [mm^{-1}]	3.673
F(000)	1220
abs corr	empirical
T_{min}/T_{max}	0.5577/0.6273
θ range [deg]	2.60 to 30.33
index ranges	$-19 < h < 19$
	$-19 < k < 19$
	$-20 < l < 20$
no. of reflns collected	27290
no. of ind reflns	12450 [R(int) = 0.1016]
completeness to θ	30.33°, 90.7%
refinement method	Full-matrix, least-squares on F^2
no. of data/restraints/params	12450/0/483
extinction coefficient	0.0031 (5)
final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0827, *wR*2 = 0.2169
R indices (all data)	*R*1 = 0.1455, *wR*2 = 0.2718
Goodness-of-fit on F^2	1.067
largest diff peak and hole [e Å^{-3}]	5.384 and −7.035

Table 3. Selected bond lengths [Å] and angles [°] for **4**

Selected bond lengths [Å][a]	selected angles [°][a]
W(1)−C(1) 1.82(2)	W(1)−C(1)−C(2) 169(1)
C(1)−C(2) 1.48(2)	P(1)−W(1)−P(2) 77.0(1)
W(1)−P(1) 2.458(4)	P(3)−W(1)−P(2) 98.8(1)
W(1)−P(2) 2.664(4)	P(4)−W(1)−P(2) 94.0(1)
W(1)−P(3) 2.474(4)	P(4)−W(1)−P(3) 77.7(1)
W(1)−P(4) 2.566(4)	P(1)−W(1)−P(3) 172.2(1)
W(1)−C(11) 1.97(2)	P(1)−W(1)−P(4) 95.8(1)
C(11)−O(11) 1.17(2)	C(1)−W(1)−P(1) 87.7(5)
Ru(1)−Ru(2) 2.829(2)	C(1)−W(1)−P(4) 102.7(5)
Ru(1)−Ru(3) 2.833(2)	C(1)−W(1)−P(3) 98.0(5)
Ru(2)−Ru(3) 2.816(1)	C(1)−W(1)−P(2) 158.4(4)
	C(1)−W(1)−C(11) 87.4(6)
	C(11)−W(1)−P(1) 93.7(5)
	C(11)−W(1)−P(3) 92.0(5)
	C(11)−W(1)−P(4) 166.4(4)
	C(11)−W(1)−P(2) 78.6(4)
	O(11)−C(11)−W(1) 175(1)
	Ru(2)−Ru(1)−Ru(3) 59.64(5)
	Ru(3)−Ru(2)−Ru(1) 60.26(5)
	Ru(2)−Ru(3)−Ru(1) 60.10(5)

[a] See Figure 2 for atom designations.

This observed high propensity towards carbonyl insertion into the W−H bond resembles that found for metallocene hydride compounds with early transition metal centres.[29]

Experimental Section

General: All manipulations of air-sensitive compounds were carried out either in a Braun Labstar glovebox under nitrogen (dried if appropriate) by conventional Schlenk techniques. Solvents were dried with appropriate drying agents[30] and freshly distilled under nitrogen prior to use. The different transition metal carbonyl compounds $Fe(CO)_5$ (Alfa products), $Re_2(CO)_{10}$ (Fluka), and $Ru_3(CO)_{12}$ (Aldrich) were commercial products and used as received. The deuterated solvents (C_6D_6, [D_8]toluene, and [D_8]THF) were also obtained from commercial suppliers and distilled from appropriate drying agents and vacuum transferred for storage in Schlenk flasks fitted with Teflon stopcocks. The dmpe ligand was synthesized by following modified literature procedures.[31] − ^{1}H, ^{13}C, and ^{31}P NMR spectra were run either on a Varian Gemini 300 spectrometer operating at 300, 75.4, and 121.5 MHz, respectively, or on a Bruker DRX 500 spectrometer at 500.2, 125.8, and 202.5 MHz, respectively. Values of δ(^{1} H), δ(^{13}C), relative to $SiMe_4$, δ(^{31}P) relative to 85% H_3PO_4. − Mass spectra (EI or FAB) were recorded on a Finnigan MAT 8230 mass spectrometer. − IR spectra: Bio-Rad FTS-45 instrument. − Elemental analyses: LECO CHNS-932 machine. − The simulation of the ^{31}P{^{1}H} NMR spectrum was carried out with the aid of the gNMR 4.1 program. The optimal fit was attained by simultaneous iteration of the chemical shifts and coupling constants.

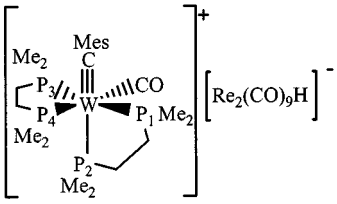
Preparation of *trans*-W(CMes)(dmpe)$_2$(H) (1): The synthesis of **1** has already been published elsewhere.[2] Only the spectroscopic data for **1** are given here. − ^{1}H NMR (C_6D_6, 298 K): δ = 6.72 (s, 2 H, Mes), 2.62 (s, 6 H, 2CH_3-Mes), 2.05 (s, 3 H, CH_3-Mes), 1.67 (s br, 12 H, PMe), 1.52 (m br, 4 H, PCH_2), 1.46 (s br, 12 H, PMe′), 1.42 (m br, 4 H, PCH_2′), −6.58 (quint, $^2J_{HP}$ = 32 Hz, $^1J_{HW}$ = 31 Hz, 1 H, WH). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ = 24.4 (s, $^1J_{PW}$ = 281 Hz). ^{13}C {^{1}H} NMR (C_6D_6, 298 K): δ = 260.4 (quint, $^2J_{CP}$ = 10 Hz, CMes), 151.5 (s, *ipso*-Mes), 137.4 (s, *o*-Mes), 135.4 (s, *p*-Mes), 130.8 (s, *m*-Mes), 34.0 (quint, PCH_2), 27.8 (m, PMe), 25.4 (m, PMe′), 22.6 (s, 2CH_3-Mes), 21.5 (s, CH_3-Mes). ^{183}W{^{1}H} NMR ([D_8]toluene, 298 K): δ −1612 (pseudo-q, $^1J_{WP}$ = 281 Hz). MS (FAB, toluene): *m*/*z* = 615 [M$^+$], 310 (M$^+$ − 2dmpe). − $WC_{22}H_{44}P_4$ (615.73): calcd. C 42.87, H 7.15%; found C 42.67, H 7.28%.

Preparation of *trans*-W{(μ-OCH)[Fe(CO)$_4$]}(CMes)(dmpe)$_2$ (2): Compound **1** (30 mg, 0.0487 mmol) was dissolved in THF (5 mL) and $Fe(CO)_5$ (6.6 μL, 0.0487 mmol) added by microsyringe. The mixture was stirred for a few minutes at room temperature. After this period, the solvent was evaporated in vacuo and the precipitate recrystallised from a diethyl ether solution at −30 °C to afford **2** as orange crystals. Yield: 33 mg (84%). − IR (cm^{-1}, THF): 2045, 1967, 1932 [Fe(CO)$_4$], 1576 (formyl), 894 (CMes). − ^{1}H NMR ([D_8]THF, 298 K): δ = 13.67 (s, 1 H, OC*H*), 6.53 (s, 2 H, Mes), 2.25 (s, 6 H, 2CH_3-Mes), 1.94 (s, 3 H, CH_3-Mes), 1.40 (m br, 4 H, PCH_2), 1.34 (s br, 12 H, PMe), 1.28 (m br, 4 H, PCH_2′), 1.20 (s br, 12 H, PMe′). − ^{31}P{^{1}H} NMR ([D_8]THF, 298 K): δ = 32.2 (s, $^1J_{PW}$ = 288 Hz). − ^{13}C{^{1}H} NMR ([D_8]THF, 298 K): δ = 298.6 (q, $^3J_{CP}$ = 5 Hz, O*C*H), 275.3 (quintet, $^2J_{CP}$ = 10 Hz, CMes), 218.5 [s, Fe(CO)$_4$], 151.2 (s, *ipso*-Mes), 135.2 (s, *o*-Mes), 133.1 (s, *p*-Mes), 128.3 (s, *m*-Mes), 33.5 (m, $^1J_{CP}$ = 10 Hz, PCH_2), 22.2 (s, 2CH_3-Mes), 22.1 (m, $^1J_{CP}$ = 7 Hz, PMe), 20.4 (s, CH_3-Mes), 17.4 (m,

$^1J_{CP}$ = 7 Hz, PMe′). − $C_{27}H_{44}P_4O_5FeW$ (811.58): calcd. C 39.92, H 5.42%; found C 40.21, H 4.90%.

Preparations of *trans*-W{(μ-OCH)[$Re_2(CO)_9$]}(CMes)(dmpe)$_2$ (3a) and [W(CMes)(CO)(dmpe)$_2$]$^+$[$Re_2(CO)_9H$]$^-$ (3b): Compound **1** (30 mg, 0.0487 mmol) was dissolved in THF (5 mL), $Re_2(CO)_{10}$ (32 mg, 0.0487 mmol) was added, and the mixture was stirred for a few minutes at room temperature. After this period, NMR examination in [D_8]THF already showed a spectroscopically small amount (36%) of **3a**. After two days at room temperature, the amount of **3a** was about 67%. − IR (cm^{-1}, THF): 1535 (ReCHO). − ^{1}H NMR ([D_8]THF, 298 K): δ = 14.98 (s, 1 H, OC*H*), 6.50 (s, 2 H, Mes), 2.31 (s, 6 H, 2CH_3-Mes), 1.91 (s, 3 H, CH_3-Mes), large multiplets for the dmpe ligands between δ = 1.40 and 1.20. − ^{31}P{^{1}H} NMR ([D_8]THF, 298 K): δ = 29.9 (s, $^1J_{PW}$ = 287 Hz). − ^{13}C{^{1}H} NMR ([D_8]THF, 298 K): selected data: δ = 295.1 (Re-*C*HO), 205.1, 202.5, 195.4, 191.5 (Re-CO).

After one week at room temperature, an almost quantitative yield of **3b** was observed spectroscopically, and recrystallisation from a saturated diethyl ether solution gave a final yield of 72%.



3b

IR (cm^{-1}, THF): 2086, 2028, 1974, 1925, 1895 ($Re_2(CO)_9H^-$), 1915 (W−CO), 891 (CMes). − ^{1}H NMR ([D_8]THF, 298 K): δ = 6.71 (s, 2 H, Mes), 2.51 (s, 6 H, 2CH_3-Mes), 2.01 (s, 3 H, CH_3-Mes), series of large multiplets for the dmpe ligands between δ = 1.87 and 1.34, −17.47 (s, Re-H). − ^{31}P{^{1}H} NMR ([D_8]THF, 298 K): δ = 16.8 (ddd, $^2J_{P3,P4}$ = 5 Hz, $^2J_{P3,P2}$ = 21 Hz, $^2J_{P3,P1}$ = 63 Hz, $^1J_{P3,W}$ = 249 Hz, P3), 14.4 (dd, $^2J_{P1,P3}$ = 65 Hz, $^2J_{P1,P4}$ = 20 Hz, $^1J_{P1,W}$ = 294 Hz, P1), 8.2 (ddd, $^2J_{P4,P1}$ = 20 Hz, $^2J_{P4,P2}$ = 25 Hz, $^2J_{P4,P3}$ = 5 Hz, $^1J_{P4,W}$ = 202 Hz, P4), −15.5 (dd, $^2J_{P2,P3}$ = 21 Hz, $^2J_{P2,P4}$ = 23 Hz, $^1J_{P2,W}$ = 35 Hz, P2). − ^{13}C{^{1}H} NMR ([D_8]THF, 298 K): δ = 293.7 (m, CMes), 230.0 (m, $^2J_{C,P4}$ = 11 Hz, W-CO), 202.2, 201.9, 199.8, 198.7, 190.5 (5s, $Re_2(CO)_9H^-$), 147.0 (s, *ipso*-Mes), 139.2 (s, *o*-Mes), 138.3 (s, *p*-Mes), 129.3 (s, *m*-Mes), 12 multiplets between δ = 32 and 14 for the 12 different carbon atoms in the dmpe ligands, 21.6 (s, 2CH_3-Mes), 20.9 (s, CH_3-Mes). − $C_{32}H_{44}P_4O_{10}Re_2W{\cdot}1/2Et_2O$ (1305.13): calcd. C 30.34, H 3.75%; found C 30.82, H 3.40%.

Preparation of [W(CMes)(CO)(dmpe)$_2$]$^+$ [$Ru_3(CO)_{11}H$]$^-$ (4): A mixture of **1** (30 mg, 0.0487 mmol) and $Ru_3(CO)_{12}$ (31.10 mg, 0.0487 mmol) in THF (5 mL) was stirred for 1 hour at room temperature. After this period, the solvent was evaporated in vacuo and the precipitate recrystallised at −30 °C from a diethyl ether solution to afford **4** as brown microcrystals. Yield: 24.6 mg (82%). − IR (cm^{-1}, THF): 2073, 2014, 1987, 1952 ($Ru_3(CO)_{11}H^-$), 1900 (W−CO), 892 (CMes). − ^{1}H NMR ([D_8]THF, 298 K): δ = 6.49 (s, 2 H, Mes), 2.27 (s, 6 H, 2CH_3-Mes), 1.90 (s, 3 H, CH_3-Mes), series of large multiplets for the dmpe ligands between δ = 1.47 and 1.08, −12.05 (s, Ru-H). − ^{31}P{^{1}H} NMR ([D_8]THF, 298 K): δ = 15.9 (ddd, $^2J_{P3,P1}$ = 66 Hz, $^2J_{P3,P2}$ = 20 Hz, $^2J_{P3,P4}$ = 6 Hz, $^1J_{P3,W}$ = 269 Hz, P3), 13.9 (dd, $^2J_{P1,P3}$ = 65 Hz, $^2J_{P1,P4}$ = 19 Hz, $^1J_{P1,W}$ = 283 Hz, P1), 7.8 (ddd, $^2J_{P4,P1}$ = 19 Hz, $^2J_{P4,P2}$ = 25 Hz, $^2J_{P4,P3}$ = 6 Hz, $^1J_{P4,W}$ = 223 Hz, P4), −15.6 (dd, $^2J_{P2,P3}$ = 20 Hz, $^2J_{P2,P4}$ = 25 Hz, $^1J_{P2,W}$ = 20 Hz, P2). − ^{13}C{^{1}H} NMR ([D_8]THF, 298 K): δ = 292 (m, CMes), 229.1 (m, W-CO), 211 (s), 205 (s), 203 (s), 198 (s) $Ru_3(CO)_{11}H^-$, 146.0 (s, *ipso*-Mes), 138.2 (s, *o*-Mes), 134.1 (s, *p*-Mes), 130.5 (s, *m*-Mes), 12 multiplets between δ = 36 and 15 for the 12 different carbon atoms in the dmpe ligands, 22.6 (s, 2CH_3-Mes), 20.1 (s, CH_3-Mes). − $C_{34}H_{44}P_4O_{12}Ru_3W$ (1254.34): calcd. C 32.51, H 3.51%; found C 32.31, H 3.70%.

Crystallography: Single crystals of **4**, of rather poor quality for X-ray studies, were obtained directly from the preparation as described in the Experimental Section. A dark red crystal of **4** with dimensions 0.18 × 0.17 × 0.14 mm was selected and mounted on the top of a glass fibre covered with a small amount of hydrocarbon oil and immediately placed on the goniometer of a Stoe IPDS diffractometer. The radiation used was Mo-*Kα* (0.71073), monochromatised by a crystal of graphite [the crystal-to-image plate distance was set to 50 mm (θmax = 30.33°)]. Because of the long exposure time, the -oscillation scan mode was selected and a total of 223 images were collected at 183 K. Each exposure required 10 min. and covered 0.9° in . The intensities were integrated after using a dynamic peak profile analysis, and estimated mosaic spread check was performed to prevent overlapping intensities. 7998 reflections were selected out of the whole limiting sphere for the cell parameter refinement. A total of 27290 reflections were collected, of which 12450 reflections were unique (*R*int = 0.1016). A numerical absorption correction based on measured crystal faces was applied without any improvement. Therefore, an empirical absorption correction utilising the program (ABSCOR)[32] was considered (maximum and minimum values of the transmission factor were 0.6273 and 0.5577).

Compound **4** crystallised in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods and difference Fourier synthesis (SHELXS-97)[33] and refined on F^2 by full-matrix, least-squares techniques (SHELXL-97).[33] All non-hydrogen atoms were refined with anisotropic thermal parameters, except C30 which resulted as non-positive definite. All hydrogen atom positions on the ligands were calculated assuming idealised geometries. The position of the hydride was found in a difference Fourier synthesis, but its position could not be refined. It was added as a constant contribution without refinement. At convergence, *R*1 = 0.0827, *wR*2 = 0.2169 and GooF = 1.067 for 483 variables refined using 12450 unique data.

Supplementary Material: Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No 150504 for compound **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk].

Acknowledgments

Financial support for this work from the Swiss National Science Foundation and from the University of Zürich is gratefully acknowledged.

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Received October 6, 2000
[I00375]