ORGANOMETALLICS

A tris-chelating oxygen ligand stabilizing the W2(CO)4(W.tplbond.W) fragment. Synthesis and crystal structure of L2W2(CO)4 L- = [(C5H5)Co{P(O)(OC2H5)2}3]-)

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compared to that obtained in diazoalkanes,[1,12] but such values have already been observed in metal–nitrogen complexes and are a consequence of the thermal vibration of the nitrogen atoms.[13] MeI adds oxidatively trans, as usual in nonpolar solvent.[14]

Note that $LiC(N_2)SiMe_3$ does not react with $RhCl(PPh_3)_3$, but it is still not known whether steric or electronic effects are dominant. Thermolysis or photolysis of **2** gives rise to several rhodium species of which $RhIMe_2(PMe_3)_3$[15] is the major product.

In conclusion, the synthetic preparative method commonly used to prepare the rhodium methyl species can be extended to diazomethane complexes. Work is now in progress to study the extension of this result to other metals and to other α heavier main-group-element diazo ligands.

Acknowledgment. We thank the Centre National de la Recherche Scientifique for a Research Fellowship (P.D.) and Dr. F. Dahan for helpful discussions.

Supplementary Material Available: Tables of refined temperature factors, final fractional coordinates, and fixed coordinates of the hydrogen atoms (3 pages); a listing of observed and calculated structure factors amplitudes (6 pages). Ordering information is given on any current masterhead page.

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[12] Cowie, M.; Gauthier, M. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1981, *B37*, 1862.

[13] Hoffman, P. R.; Yoshida, T.; Okano, T.; Otsuka, S.; Ibers, J. A. *Inorg. Chem.* 1976, *15*, 2462.

[14] Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977; Chapter 16, p 941.

[15] Thorn, D. L. *Organometallics* 1985, *4*, 192. The yield of $RhI(Me)_2(PMe_3)_3$ depends on the reaction conditions and especially on the solvent. It is higher than 50% in $CDCl_3$. Experiments are now in progress to determine the origin of the second methyl group. Two other rhodium complexes have been characterized by phosphorus NMR (A_2B spectrum) during the thermolysis, but not isolated. The trimethylsilyl substituent is involved in the thermolysis process, and work is going on to determine the nature of the resulting silyl species.

A Tris-Chelating Oxygen Ligand Stabilizing the $W_2(CO)_4(W{\equiv}W)$ Fragment. Synthesis and Crystal Structure of $L_2W_2(CO)_4$ ($L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$)

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Summary: From the reaction of $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$ (NaL) with $W(CO)_6$ in refluxing diglyme the dark red crystalline compound $[L_2W_2(CO)_4]$ has been obtained. The crystal structure determination shows that the tris-chelating oxygen ligands L^- coordinate each to one tungsten center. The four carbonyls are bent back over the tungsten–tungsten triple bond to form linear-type asymmetric bridges. NMR and IR data indicate that the solid-state structure is retained and is relatively rigid in solution.

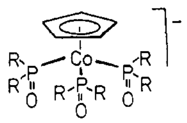

Figure 1. Schematic representation of the oxygen tripod ligand L^- ($R = OC_2H_5$).

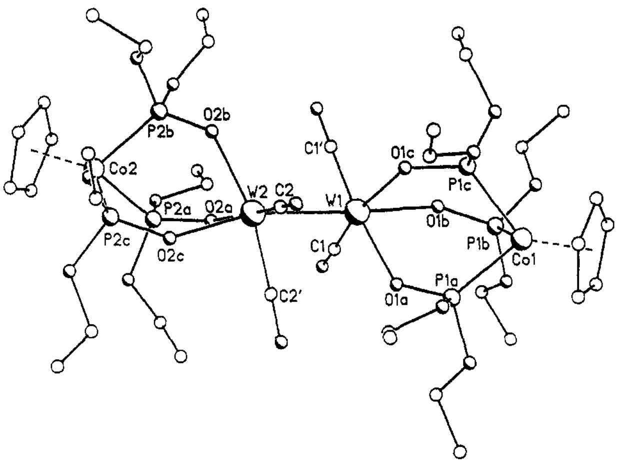

Figure 2. Crystal structure of $[L_2W_2(CO)_4]$ ($L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$).

The anion (cyclopentadienyl)tris(diethyl phosphito)cobaltate(1−), hereafter abbreviated as L^-, has a strong tendency to act as an O,O,O-tripod ligand by using the oxygen atoms of the three $R_2P{=}O$ functional groups as donor centers (see Figure 1). It forms stable complexes with metal ions in high as well as in low oxidation states.[1] We have recently observed that the metal(0) complexes $[LM(CO)_3]^-$ (M = Cr, Mo, W)[2] are useful starting compounds for the synthesis of a variety of hydride and alkyl complexes $[LM(CO)_3R]$ (R = H, alkyl) and of nitrosyl and allyl complexes $[LM(CO)_2R']$ (R′ = NO, η^3-allyl). No other oxygen ligands are known to stabilize such a broad range of organometallic fragments.[3] It seemed therefore interesting to further explore the organometallic chemistry of this ligand. We have now prepared the tungsten–tungsten triply bonded dimer $[L_2W_2(CO)_4]$, the first metal complex of L containing a multiple metal–metal bond. It may be noted that the only other complexes containing the $W_2(CO)_4$ unit are the cyclopentadienyl complexes $[(C_5R_5)_2W_2(CO)_4]$ (R = H,[4] CH_3[5]). Of the various attempts to synthesize the title compound according to the synthesis of the analogous complexes $[(C_5R_5)_2M_2(CO)_4]$, neither thermolysis or photolysis nor aerial oxidation of $[LW(CO)_3H]$ has led, in our hands, to $[L_2W_2(CO)_4]$. This compound is, however, accessible in one step in moderate yields from NaL and hexacarbonyl tungsten in refluxing diglyme.[6] A crystal structure determination[7] revealed the

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[1] Kläui, W.; Müller, A.; Eberspach, W.; Boese, R.; Goldberg, I. *J. Am. Chem. Soc.* 1987, *109*, 164.

[2] Kläui, W.; Müller, A.; Scotti, M. *J. Organomet. Chem.* 1983, *253*, 45.

[3] Examples of metal carbonyl hydride complexes containing only oxygen donors as additional ligands are probably the tetrameric units $[\{(HO)M(CO)_3H\}_4]$ (M = Mo, W): Sartorelli, U.; Garlaschelli, L.; Ciani, G.; Bonora, G. *Inorg. Chim. Acta* 1971, *5*, 191.

[4] Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* 1977, *23*, 85.

[5] King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* 1979, *171*, 53.

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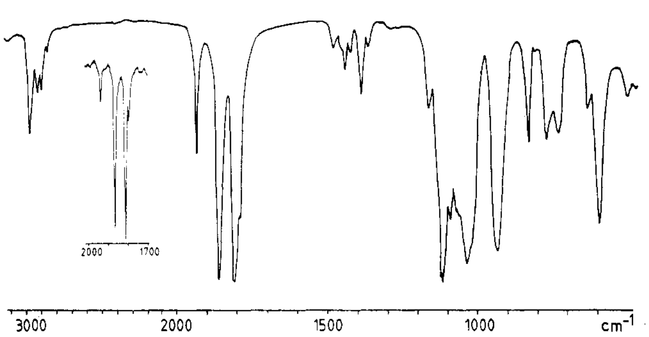

Figure 3. IR spectra of $[L_2W_2(CO)_4]$ in KBr and hexane (insert).

molecular structure of $[L_2W_2(CO)_4]$ shown in Figure 2. The oxygen tripod ligand L^- itself can be described as a cobalt complex. The P–Co–P angles are 90 ± 1° as found in other complexes of L^- as well.[8] The P–O(–W) bond lengths (average = 1.50 Å) are shorter than the P–O(–C) distances (average = 1.59 Å) and lie in the range between P–O single and double bonds. Accordingly, we find relatively large P–O–W angles (average = 134.5°). All other bond lengths and angles within L are as expected. The overall symmetry of $[L_2W_2(CO)_4]$ is roughly C_i. The coordination at the tungsten atoms is distorted octahedral[9] with each of the three oxygen donor atoms of L being approximately trans to the carbon monoxide ligands and the second tungsten center, respectively. The $W\equiv W$ distance of 2.503 (1) Å is comparable to the $Mo\equiv Mo$ distance of 2.507 (1) Å in $[(HBpz_3)_2Mo_2(CO)_4]$.[10] It is longer than other tungsten–tungsten triple bonds[11] but much shorter than the tungsten–tungsten single-bond distance of 2.99 Å in $[(C_5H_5)_2W_2(CO)_4(HC\equiv CH)]$.[12] All four carbonyls in $[L_2W_2(CO)_4]$ are bent back over the tungsten–tungsten bond to form linear-type asymmetric bridges. There are two pairs of carbon monoxide ligands (C(1)O, C(2)O and C(1′)O, C(2′)O), each defining approximately a plane. The dihedral angle between the two planes is 98.1°. Two carbonyls (1′ and 2) have shorter W–C distances (average = 1.91 ± 0.01 Å) and more acute W–W–C angles (average = 74.7 ± 0.5°) than the other two (average W–C = 1.96 ± 0.01 Å; average W–W–C = 78.8 ± 0.4°). A very similar pairwise arrangement of CO ligands has been found in $[(HBpz_3)_2Mo_2(CO)_4]$.[10,13] The shorter W–C distances coincide with slightly shorter W–O distances trans to W–C (2.146 (7) vs. 2.173 (7) Å). The W–O distances trans to $W\equiv W$ are significantly longer (average = 2.21 ± 0.01 Å). The angles L(c)–W–W are 151.9 and 153.7° (L(c) denotes the center of the three oxygen donor atoms). They may be compared with the corresponding angles of 180° in $[(C_5H_5)_2Mo_2(CO)_4]$[14] and 168.3° in $[(C_5Me_5)_2Mo_2(CO)_4]$.[15] It is not at all clear what are the electronic prerequisites of ligands which are able to stabilize the $M_2(CO)_4$ units and how these electronic properties govern the geometry of the ligand–M–M–ligand axis. It is interesting, however, to note the pronounced chemical differences[16] between the linear $[(C_5H_5)_2Mo_2(CO)_4]$ and the bent $[(C_5Me_5)_2Mo_2(CO)_4]$. Unfortunately, the structures of the corresponding tungsten compounds have not, to our knowledge, been reported.

The structure of $[L_2W_2(CO)_4]$ in solution is probably very similar to the solid-state structure. The broad asymmetric signal of the OCH_2 protons in the ^1H NMR spectrum shows that the oxygen tripod ligands L^- do not rotate about the cobalt–tungsten axis. Such a nonrigidity on the NMR time scale would lead to a symmetric 13-line multiplet signal of the OCH_2 protons as observed in complexes with C_{3v} symmetry like $[LW(CO)_3]^-$ and fluxional molecules like $[LW(CO)_3I]$.[1]

The IR spectra of $[L_2W_2(CO)_4]$ show four bands in the ν_{co} region; two of them are very strong (see Figure 3).[17] The similarity of the solution and the solid-state spectra is in accord with the persistence of the one isomer in solution. The frequencies of the two strong bands (1865 and 1811 cm^{-1} in hexane) may be compared with the ones reported for $[(C_5H_5)_2W_2(CO)_4]$ (1885 and 1830 cm^{-1} in isooctane)[4] and $[(C_5Me_5)_2W_2(CO)_4]$ (1874 and 1828 cm^{-1} in tetradecane).[5] The data indicate that the oxygen ligand L^- induces more back-bonding than $C_5H_5^-$ and $C_5Me_5^-$. We observe this behavior in all molybdenum and tungsten complexes prepared so far. We assume however not that L^- is a particularly strong σ-donor but that it is a good π-donor since the ligand field spectra of $[CoL_2]$, $[NiL_2]$, and $[CuL_2]$ characterize L^- as a strikingly weak ligand.[18] Its position in the spectrochemical series is near fluoride and oxide. How much this dominates the chemistry of the tungsten–tungsten triple bond remains to be seen.

Supplementary Material Available: Tables of the atomic

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(6) Preparation of $[L_2W_2(CO)_4]$: 2.5 g (7.1 mmol) $W(CO)_6$ and 4.0 g (7.2 mmol) NaL were heated under an atmosphere of nitrogen in 10 mL of diglyme for 4 h to 180 °C. Water and dichloromethane were added to the cooled reaction mixture, and the aqueous phase was extracted with more dichloromethane. The combined organic phases were evaporated to dryness, and the solid residue was chromatographed on alumina with dichloromethane. Recrystallization from methanol gave 688 mg (0.44 mmol, 12%) of shiny dark red to black crystals of $[L_2W_2(CO)_4]$. The air-stable compound is soluble in tetrahydrofuran, acetone, and chlorinated hydrocarbons, only slightly soluble in ethanol and pentane, and insoluble in water. Anal. Calcd for $C_{38}H_{70}Co_2O_{22}P_6W_2$: C, 29.44; H, 4.55. Found: C, 29.14; H, 4.50. ^1H NMR (60 MHz, $CDCl_3$): δ 1.2 (t, ^3J(HCCH) = 7 Hz, 36, $POCH_2CH_3$), 3.7–4.4 (asym m, 24, $POCH_2$), 4.8 (s, 10, C_5H_5). IR (KBr): 1932 (m), 1855 (vs), 1803 (vs), 1790 (sh) (ν_{co}), 1111 (vs) ($\nu_{p=o}$), 591 (s) ($\delta_{p=o}$) cm^{-1}. IR (CH_2Cl_2): 1928 (m), 1850 (vs), 1797 (vs), 1777 (sh) (ν_{co}) cm^{-1}.

(7) Crystal data: $C_{38}H_{70}Co_2O_{22}P_6W_2$, M_r 1550.4, dark red prisms, monoclinic, space group $P2_1/c$, a = 14.815 (2) Å, b = 26.000 (3) Å, c = 15.500 (2) Å, β = 105.50 (1)°, V = 5753.3 Å^3, Z = 4, D_{calcd} = 1.790 g·cm^{-3}, $F(000)$ = 3064, μ(Mo Kα) = 4.87 mm^{-1}; Stoe-Siemens four-circle diffractometer, crystal dimensions 0.7 × 0.5 × 0.2 mm^3, 10090 unique reflections ($2\theta_{max}$ = 50°), 7282 with $|F| > 4\sigma(F)$ treated as observed, empirical absorption correction (R_{int} = 0.039 for 357 azimuthal scans); structure solved by Patterson and Fourier methods, blocked-cascade refinement (on F) of 493 parameters, non-hydrogen atoms (except ethyl groups) anisotropic, riding model employed for H atoms with C–H = 0.96 Å, Cp rings idealized, weighting scheme $1/w = \sigma^2(F) + 0.0006F^2$, final R = 0.059 (wR = 0.068), all calculations performed with SHELXTL.

(8) See e.g.: Dubler, E.; Linowsky, L.; Kläui, W. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 191. Kläui, W.; Scotti, M.; Valderrama, M.; Rojas, S.; Sheldrick, G. M.; Jones, P. G.; Schröder, T. *Angew. Chem.* **1985**, *97*, 697; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 683.

(9) O(1a)–W(1)–C(1′) = 173.4 (4)°; O(2a)–W(2)–C(2) = 171.3 (4)°; O(1c)–W(1)–C(1) = 164.8 (4)°; O(2b)–W(2)–C(2′) = 165.8 (3)°; O(1b)–W(1)–W(2) = 159.0 (2)°; O(2c)–W(2)–W(1) = 156.5 (2)°.

(10) Curtis, M. D.; Shiu, K.-B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335.

(11) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

(12) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

(13) In $[(HBpz_3)_2Mo_2(CO)_4]$ the differences in M–M–C angles between the two sets of CO ligands are more pronounced whereas the differences in M–C bond lengths are larger in $[L_2W_2(CO)_4]$. The exact nature of the bonding of such linear semibridging carbonyls has been scrutinized in recent years. Fenske–Hall molecular orbital calculations indicate that they act as π-acceptors, not π-donors as previously suggested. They bend over the $M\equiv M$ bond in order to accept electrons from the metal–metal π-bonds. See e.g.: Morris-Sherwood, B. J.; Powell, C. B.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 5079.

(14) Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034.

(15) Huang, J.-S.; Dahl, L. F. *J. Organomet. Chem.* **1983**, *243*, 57.

(16) See ref 15 and references cited therein.

(17) The IR spectra of compounds containing the ligand L^- all show the same typical pattern with only the $\nu_{p=o}$ and $\delta_{p=o}$ bands being sensitive to the metal ion coordinated to L^-. For a detailed discussion see: Kläui, W.; Dehnicke, K. *Chem. Ber.* **1978**, *111*, 451.

(18) Kläui, W.; Eberspach, W.; Gütlich, P. *Inorg. Chem.*, submitted for publication.

coordinates, bond lengths and angles, and thermal parameters (8 pages); a listing of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

New Types of Remarkably Stable Alkyl Hydride Complexes of Tungsten[1]

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Summary: Remarkably thermally stable alkyl hydride complexes of tungsten result from the treatment of $\mathrm{Cp'W(NO)(CH_2SiMe_3)_2}$ [$\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5H_5}$ (Cp) or $\eta^5\text{-}\mathrm{C_5Me_5}$ (Cp*)] with elemental hydrogen under differing experimental conditions. At low pressures of $\mathrm{H_2}$ (e.g. 80 psig) in the presence of Lewis bases, L, the monometallic complexes $\mathrm{Cp'W(NO)(H)(CH_2SiMe_3)(L)}$ [$\mathrm{L} = \mathrm{P(OPh)_3}$, $\mathrm{PMePh_2}$, or $\mathrm{PMe_3}$] are formed in moderate yields. At higher pressures of $\mathrm{H_2}$ (e.g. 920 psig) in the absence of L's, $\mathrm{Cp^*W(NO)(CH_2SiMe_3)_2}$ is converted to a mixture of the bimetallic complexes, $\mathrm{[Cp^*W(NO)(H)]_2(\mu\text{-}H)_2}$ and $\mathrm{[Cp^*W(NO)H](\mu\text{-}H)_2[Cp^*W(NO)(CH_2SiMe_3)]}$, which are separable by fractional crystallization.

Transition-metal alkyl hydride complexes have been invoked as intermediates in many homogeneously catalyzed processes.[2] However, the paucity of such compounds that are sufficiently thermally stable to be isolable has severely hampered the study of their chemistry as discrete complexes.[3] We now wish to report that new types of remarkably stable alkyl hydride complexes of tungsten result from the treatment of 16-electron $\mathrm{Cp'W(NO)(CH_2SiMe_3)_2}$ [$\mathrm{Cp'} = \eta^5\text{-}\mathrm{C_5H_5}$ (Cp) or $\eta^5\text{-}\mathrm{C_5Me_5}$ (Cp*)][4] with elemental hydrogen under differing experimental conditions.

Hydrogenation at 80 psig of $\mathrm{CpW(NO)(CH_2SiMe_3)_2}$ in the presence of 1 equiv of a Lewis base, L, affords moderate yields (~60%) of $\mathrm{CpW(NO)(H)(CH_2SiMe_3)(L)}$ complexes, i.e., eq 1. The alkyl hydride products of conversions 1 are

$$\mathrm{CpW(NO)(CH_2SiMe_3)_2 + L + H_2\ (80\ psig)} \xrightarrow[20\ ^\circ\mathrm{C},\ 3\ \mathrm{h}]{\text{hexanes}} \mathrm{CpW(NO)(H)(CH_2SiMe_3)(L) + Me_4Si} \qquad (1)$$

$$\mathbf{1},\ \mathrm{L = P(OPh)_3}$$
$$\mathbf{2},\ \mathrm{L = PMePh_2}$$

isolable by recrystallization from $\mathrm{CH_2Cl_2}$/hexanes as yellow, microcrystalline solids[5] which are stable in air at 0 °C and under $\mathrm{N_2}$ at 20 °C for at least 6 months. They are only slightly soluble in hexanes and $\mathrm{Et_2O}$ but quite soluble in more polar organic solvents to form mildly air-sensitive solutions. In $\mathrm{C_6D_6}$ at 50 °C, **1** eliminates $\mathrm{Me_4Si}$ and transforms quantitatively (by ^{1}H NMR) into the ortho-metalated compound **3**,[5] i.e., eq 2. The solid-

$$\underset{\mathbf{1}}{\mathrm{CpW(NO)(H)(CH_2SiMe_3)[P(OPh)_3]}} \xrightarrow[50\ ^\circ\mathrm{C},\ 12\ \mathrm{h}]{\mathrm{C_6D_6}} \underset{\mathbf{3}}{\mathrm{CpW(NO)(H)[P(OPh)_2(OC_6H_4)]}} + \mathrm{Me_4Si} \qquad (2)$$

state molecular structure of **3** was confirmed by a single-crystal X-ray crystallographic analysis.[6]

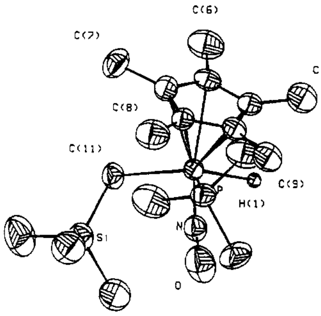

Figure 1. Molecular structure of $\mathrm{Cp^*W(NO)(H)(CH_2SiMe_3)(PMe_3)}$ (**4**). Hydrogen atoms other than the hydride have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W–P = 2.494 (2), W–N = 1.771 (5), W–C(11) = 2.248 (6), W–H(1) = 1.75, W–Cp* = 2.042, N–O = 1.223 (7), P–W–N = 102.3 (2), P–W–C(11) = 81.1 (2), P–W–H(1) = 61.9, N–W–C(11) = 94.0 (2), N–W–H(1) = 90.1, C(11)–W–H(1) = 142.8, W–N–O = 169.1 (5).

The occurrence of reaction 2, a thermal *intramolecular* C–H bond activation, led us to investigate the possibility of **2** initiating such activation *intermolecularly*. Unfortunately, thermolysis of **2** in $\mathrm{C_6H_6}$ only results in the formation in low yields of $\mathrm{CpW(NO)(PMePh_2)_2}$[7] as the only identifiable product. Reasoning that a complex analogous to **1** and **2** but having a more electron-rich metal center would be more likely to initiate the desired C–H bond activation,[8] we next synthesized $\mathrm{Cp^*W(NO)(H)(CH_2SiMe_3)(PMe_3)}$ (**4**)[5] in 54% yield from $\mathrm{Cp^*W(NO)(CH_2SiMe_3)_2}$ (cf. eq 1). A single-crystal X-ray crystallographic analysis of **4**[9] revealed that it possesses a severely distorted "four-legged piano stool" molecular structure in the solid state (Figure 1), the C(11)–W–H(1) angle being 142.8°.[10] The short W–N (1.771 (5) Å) and long N–O (1.223 (7) Å) bond lengths exhibited by **4** in its essentially linear (169.1 (5)°) WNO group, as well as its low ν_{NO} ($\mathrm{CH_2Cl_2}$) of 1545 cm^{-1}, indicate considerable W→NO back-bonding[11] and greater electron density at the metal center than in **1** or **2**. Accordingly, even though the nonbonded separation between C(11) and H(1) is 3.80 Å in the solid state, thermolysis of **4** in $\mathrm{C_6H_6}$ does indeed result in the elimination of $\mathrm{Me_4Si}$ and intermolecular C–H bond activation, i.e., eq 3. Reaction 3 is quantitative (by ^{1}H

$$\mathrm{Cp^*W(NO)(H)(CH_2SiMe_3)(PMe_3) + C_6H_6} \xrightarrow{40\ ^\circ\mathrm{C},\ 22\ \mathrm{h}} \underset{\mathbf{5}}{\mathrm{Cp^*W(NO)(H)(C_6H_5)(PMe_3)}} + \mathrm{Me_4Si} \qquad (3)$$

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[1] Organometallic Nitrosyl Chemistry. 33. For part 32, see: Legzdins, P.; Richter-Addo, G. B.; Wassink, B., submitted for publication.

[2] Parshall, G. W. *Homogeneous Catalysis*; Wiley: Toronto, 1980.

[3] Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332 and references therein.

[4] Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

[5] Characterization data for all new complexes isolated are presented as supplementary material.

[6] Einstein, F. W. B.; Jones, R. H., unpublished observations.

[7] Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

[8] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245 and references therein.

[9] X-ray diffraction data for $\mathrm{Cp^*W(NO)(H)(CH_2SiMe_3)(PMe_3)}$: orthorhombic; space group *Pbca*; $a = 8.783\ (1)$ Å, $b = 17.963\ (2)$ Å, $c = 28.017\ (3)$ Å; $V = 4419.96$ Å^3; $Z = 8$; $\mu = 54.65$ cm^{-1}; diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(\mathrm{K}\alpha_1) = 0.709\,30$ Å); scan range = $3° \leq 2\theta \leq 50°$; reflections = 2492 with $I \geq 3\sigma(I)$; $R = 0.025$, $R_w = 0.034$; GOF = 1.451. All non-hydrogen atoms were refined with anisotropic thermal parameters (199 parameters).

[10] The hydride (H(1)) is situated in a plane midway between the two "trigonal" faces containing the Cp* group and C(11), P, and N, respectively.

[11] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116 and references therein.

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