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 H_2 (e.g. 80 psig) in the presence of Lewis bases, L, the monometallic complexes $\mathrm{Cp'W(NO)(H)(CH_2SiMe_3)(L)}$ [L = $\mathrm{P(OPh)_3}$, $\mathrm{PMePh_2}$, or $\mathrm{PMe_3}$] are formed in moderate yields. At higher pressures of 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

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

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

isolable by recrystallization from $\mathrm{CH_2Cl_2}$/hexanes as yellow, microcrystalline solids[5] which are stable in air at 0 °C and under 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 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-state molecular structure of 3 was confirmed by a single-crystal X-ray crystallographic analysis.[6]

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

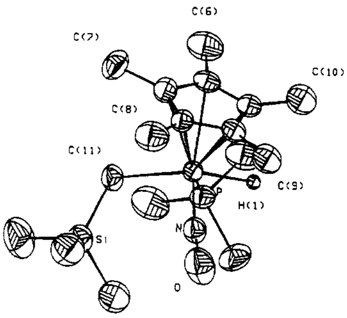

Figure 1. Molecular structure of $\mathrm{Cp^*W(NO)(H)(CH_2SiMe_3)(PMe_3)}$ (4). Hydrogen atoms other than the hydride have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W–P = 2.494 (2), W–N = 1.771 (5), W–C(11) = 2.248 (6), W–H(1) = 1.75, W–Cp* = 2.042, N–O = 1.223 (7), P–W–N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

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

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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; μ = 54.65 cm^{-1}; diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator (λ(Kα_1) = 0.709 30 Å); scan range = $3° \le 2\theta \le 50°$; reflections = 2492 with $I \ge 3\sigma(I)$; 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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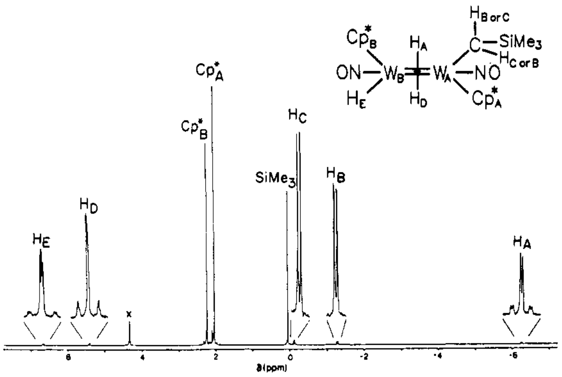
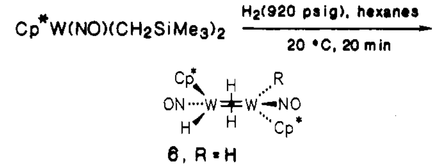


Figure 2. The 400-MHz ^1H NMR spectrum of $[Cp^*W(NO)H](\mu\text{-}H)_2[Cp^*W(NO)(CH_2SiMe_3)]$ (7) in CD_3NO_2.

NMR), and the experimental conditions employed are considerably milder than those cited in two recent reports of *thermal* benzene C–H activation by monometallic complexes.[12] Regrettably, attempts to activate the C–H bonds of CH_4, *n*-hexane, or cyclohexane by 4 in an identical manner result only in the formation of low yields of $Cp^*W(NO)(PMe_3)_2$[13] as the only identifiable product.

Hydrogenation at 80 psig of $Cp^*W(NO)(CH_2SiMe_3)_2$ without the added Lewis base of eq 1 generates a mixture of at least eight products (by ^1H NMR). When performed at 920 psig of H_2, however, the reaction is much cleaner, i.e., eq 4, the bimetallic products 6 and 7 being the principal species formed. They may be separated by repeated fractional crystallizations from toluene/hexanes. The less soluble product 6 is the Cp* analogue of $[CpW(NO)H]_2(\mu\text{-}H)_2$, a complex that we have described in great detail previously.[14] The other product 7 is novel and is isolable as a bright orange-red crystalline material whose solid and solution properties are similar to those of the mononuclear alkyl hydride complexes presented above. Its ^1H NMR spectrum is shown in Figure 2. Particularly noteworthy features of this spectrum are the chemical shifts of the hydride resonances, the bridging hydrides resonating at δ −6.36 and +5.30 and the terminal hydride resonating at δ +6.57 ppm (assigned on the basis of the intensities of the ^{183}W satellites).[14] The spectroscopic properties of 6 and 7[5] are consistent with their having the molecular structures shown in eq 4, that of 7 having been confirmed in the solid state by a single-crystal X-ray crystallographic analysis.[6] Complex 7 is thus a new member of the extremely small family of thermally stable bimetallic alkyl hydride compounds, its closest relative probably being the unsymmetrical aryl complex $\{[(Et_3P)_2PtPh](\mu\text{-}H)[PtH(PEt_3)_2]\}^+$.[15] In a formal sense, 7 is an analogue of 4, the PMe_3 ligand in the latter having been replaced by a $Cp^*W(NO)H_2$ group.



(4)

6, R = H
7, R = CH_2SiMe_3

Further studies of these alkyl hydride complexes are currently in progress.

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Supplementary Material Available: Elemental analysis and spectroscopic (IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, mass spectral) data for complexes 1–7 and tables of fractional coordinates and isotropic and anisotropic thermal parameters for 4 (6 pages); a listing of structure factors for 4 (17 pages). Ordering information is given on any current masthead page.

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[12] (a) Chetcuti, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 942. (b) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090.

[13] For Cp analogues, see: Christensen, N. J.; Hunter, A. D.; Legzdins, P.; Sánchez, L. *Inorg. Chem.*, in press.

[14] (a) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971. (b) Legzdins, P.; Martin, J. T.; Oxley, J. C. *Organometallics* **1985**, *4*, 1263.

[15] Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778.

Folding and Unfolding of a Trirhodium Chain about an Isocyanide Ligand. The Structure of $[Rh_3\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2(n\text{-}C_4H_9NC)_5CO]^{3+}$ as a Solid and in Solution

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Summary: In the solid state, $[Rh_3\{\mu\text{-}(Ph_2PCH_2)_2PPh\}_2(n\text{-}BuNC)_5CO]^{3+}$ is a tan color and possesses a bent Rh_3 chain with a triply bridging, four-electron-donating isocyanide and a bridging carbon monoxide, while in dichloromethane solution, it is blue with only terminal isocyanide ligands and a terminal carbon monoxide ligand.

The bridge/terminal interchange for two-electron-donating isocyanide (and carbon monoxide) ligands has received considerable attention.[1] However, little is known about transformations involving the other bridging modes for isocyanide ligands.[2,3] Herein we report on a novel reaction in which a triply bridging isocyanide ligand converts into a terminal isocyanide upon dissolution. The structural chemistry involved demonstrates the remarkable flexibility found in trinuclear complexes bridged by bis((diphenylphosphino)methyl)phenylphosphine (dpmp) ligands.[4]

Addition of 5 equiv of *n*-butyl isocyanide to a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-}Cl)Cl]BPh_4$[4a] produces a deep blue solution from which tan crystals of $[Rh_3(\mu\text{-dpmp})_2(CO)(n\text{-}BuNC)_5][PF_6]_3$ (1)[5] are obtained (in 50% yield) by precipitation through the addition of a methanol solution of ammonium hexafluorophosphate. In the solid state, 1 shows infrared absorptions due to terminal isocyanides at 2160 cm^{-1}, to a bridging

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[1] Adams, R. D.; Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; p 489.

[2] Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193.

[3] Exchange of four-electron, doubly bridging isocyanides with terminal isocyanides in $Ni_4(CN\text{-}t\text{-}Bu)_7$ has been reported: Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743.

[4] (a) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677. (b) Olmstead, M. M.; Guimerans, R. R.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 2473. (c) Balch, A. L.; Guimerans, R. R.; Olmstead, M. M. *J. Organomet. Chem.* **1984**, *268*, C38. (d) Balch, A. L.; Fossett, L. A.; Guimerans, R. R.; Olmstead, M. M. *Organometallics* **1985**, *4*, 781.

[5] Anal. Calcd for $C_{90}H_{103}F_{18}N_5OP_9Rh_3$: C, 49.12; H, 4.72; N, 3.18. Found: C, 48.51; H, 4.62; N, 3.07.

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