was found between 48 and 66 ppm relative to external 1,4-dioxane.[6,7] In natural abundance studies the resonance of the ring oxygen appeared considerably broader than that of the other lines[7] as a result of the more restricted rotational freedom of O-5. From another work the surprisingly low-field oxygen NMR signal at 86.0 ppm of 7-oxanorbornane was also avaialble.[8]

This prompted us to label the anomeric oxygen atom[5b] of **1a** ($H_2{}^{17}O$ 10% enrichment, in boiling dry 1,4-dioxane) and after acetylation to treat **1c** with sodium azide. The 48.8-MHz ^{17}O NMR spectrum of the resulting purified 1,4-anhydro sugar **3b**, shown in Figure 2, indicates a very broad signal at 85.9 ppm in perfect agreement with that reported for 7-oxanorbornane[8] and strongly deshielded with respect to the ring oxygen atom of monosaccharides.[6,7] This result afforded evidence for pathway b in the formation of the 1,4-anhydro sugar **3b**.

However, neither the ^{17}O chemical shift of the model 2-oxanorbornane nor the signal position of O-5 of monosaccharides in conformations other than chair was available to us. Thus, it appeared advisable to prove that the ^{17}O NMR consistency of **3b** with 7-oxanorbornane was not fortuitous.

Therefore, labeling of the anomeric oxygen atom of **1a** was also carried out with 50% enriched $H_2{}^{18}O$. After acetylation and sodium azide treatment of **1d**, the resulting 1,4-anhydro sugar **3c** was examined by 100.62-MHz ^{13}C NMR spectroscopy. After Gaussian resolution enhancement,[9] oxygen-18-induced upfield isotopic shifts[5a,5b] of 0.025 ppm were detected at the two directly attached carbon sites (99.1 and 81.9 ppm in $CDCl_3$), assigned unambiguously by specific proton decoupling[1] to C-1 and to C-4, respectively. These resonances appeared as a pair of signals corresponding to the $^{13}C–^{16}O$ and $^{13}C–^{18}O$ species. This experiment confirmed the C-1 oxy anion mechanism of pathway b in the formation of the 1,4-anhydro sugar **3c**.

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[9] Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337.

Characterization of the First Examples of Isolable Molecular Hydrogen Complexes, $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = Cy, *i*-Pr). Evidence for a Side-on Bonded H_2 Ligand

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We wish to report the first examples of isolable[1] transition-metal complexes containing a coordinated dihydrogen molecule, characterized by a variety of spectroscopic and structural methods to possess η^2-bonded H_2.

Toluene solutions of deep purple $M(CO)_3(PCy_3)_2$ (M = Mo, W)[2] react readily and cleanly with hydrogen (1 atm) precipitating yellow crystals of *mer-trans*-$M(CO)_3(PCy_3)_2(H_2)$ in 85–95% yields.[2,3] The tungsten P-*i*-Pr_3 analogue is isolated in lower yields from hexane, since it is very soluble in hydrocarbon solvents. $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ could not be obtained as a solid although reversible color changes (purple ↔ yellow) in solution indicate H_2 addition. In all complexes the H_2 is extremely labile, and storage and handling under an H_2-enriched atmosphere is necessary. Immediate discoloration occurs upon exposure of microcrystalline samples to vacuum or argon, but the original color is instantly restored upon contact with H_2. Bulk loss of H_2 from the solids is slow at 20 °C ($P_{\text{dissoc}} \cong$ 10 torr for $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ and 1 torr for the PCy_3 analogue), but the H_2 can be rapidly quantitatively removed from toluene solutions to give $M(CO)_3(PR_3)_2$ by flushing with argon or exposure to partial vacuum at 25–50 °C.

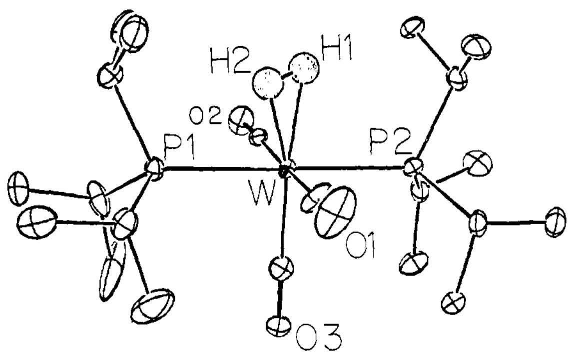

Figure 1. Geometry of the $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}H_2)$ molecule with hydrogen atoms of the P-*i*-Pr_3 groups omitted for clarity. The positions of the two hydrogen atoms shown were derived from neutron data while heavy-atom positions are from −100(5) °C X-ray data.

Suitable single crystals of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ have been subjected to X-ray and neutron diffraction analyses. Because neutron diffraction is the method of choice for locating hydrogen atoms bound to heavy metals,[4] room-temperature neutron data were collected at the Los Alamos Pulsed Neutron Source utilizing the Laue time-of-flight method and were used to produce a difference–Fourier map phased on the non-hydrogen atom coordinates from room temperature X-ray studies.[5] This route clearly demonstrated the presence of both atoms of the H_2 ligand. Location of some other hydrogen atoms in the molecule was hampered by disorder in the phosphine ligands. Attempts to obtain detailed molecular parameters by least-squares refinement were ultimately hindered by this inability to properly model the phosphine ligands.

Subsequent low-temperature [−100 (5) °C] X-ray diffraction analysis[6] confirmed the location of the molecular hydrogen ligand.[9] Refinement in this case proved more tractable, since X-ray data are less sensitive to disorder involving phosphine hydrogen atoms. The resulting geometry about the tungsten atom (Figure 1) is that of a regular octahedron with "cis" interligand angles about tungsten ranging from 88.0 (4)° to 92.0 (6)°. The dihydrogen ligand is symmetrically coordinated in an η^2 mode with average tungsten–hydrogen distances of 1.95 (23) Å (X-ray) and 1.75 Å (neutron, ΔF). The H–H separation is 0.75 (16) Å (X-ray) and

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[1] Interaction of $Cr(CO)_5$ with H_2 in a rare-gas matrix has recently been observed. (Sweany, R. L. private communication.)

[2] Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61.

[3] Anal. Calcd for $C_{39}H_{68}O_3P_2Mo$: C, 63.1; H, 9.2, P, 8.3. Found: C, 62.8; H, 9.0; P, 8.0. Calcd for $C_{39}H_{68}O_3P_2W$: C, 56.4; H, 8.3; P, 7.5. Found: C, 56.9; H, 8.5; P, 7.5.

[4] Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183.

[5] Vergamini, P. J.; Wasserman, H. J.; Kubas, G. J.; Ryan, R. R., unpublished results.

[6] $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ crystallizes in the centrosymmetric orthorhombic space group *Pcab* (No. 61) with a = 15.749 (3) Å, b = 24.219 (5) Å, c = 13.333 (3) Å, V = 5085.7 Å^3, and ρ_{calcd} = 1.54 g cm^{-3} for Z = 8 and M_r = 589.8. Automated diffraction data were collected at −100 (5) °C; the residuals for 2118 absorption corrected data [$2\theta_{\max}$ = 45°; $I > 2(\sigma)I$] are R_F = 4.3% and R_{wF} = 5.9%. All heavy atoms in the molecule were located and refined; hydrogen atoms of the P-*i*-Pr_3 groups were included in fixed positions. Weights were derived from standard counting statistics modified by an "ignorance" factor of 0.015. Calculations were performed on a CDC 7600 computer with use of local crystallographic programs developed by Dr. A. C. Larson.[7] Neutral atom scattering factors, modified by anomalous dispersion (except hydrogen), were used.[8]

[7] Larson, A. C. Abstracts, American Crystallographic Association Proceedings, 1977.

[8] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

[9] Positional parameters were refined for both hydrogen atoms as well as an isotropic thermal parameter for H(2) for which B_{iso} = 3 (4) Å^2. Refinement of an isotropic thermal parameter for H(1) resulted in $B_{\text{iso}} \sim -2(4)$ Å^2 so that in the final cycles of refinement B_{iso} for H(1) was fixed at 2.0 Å^2.

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Table I. Vibrational Frequencies (cm^{-1}) for Solid $W(CO)_3(PCy_3)_2(H_2)$ and Isotopically Substituted Species[a]

	HH	HD	DD
ν(HH)	2690 (IR)[b]	2360 (*I*R)	~1900 (R)
$\nu_a(WH_2)$	1570 (IR)	~1350 (*I*R)[b]	~1132 (*I*R)[b]
$\nu_s(WH_2)$	*953 (IR, R)*	*791 (IR, R)*	*703 (IR, R)*
$\delta(WH_2)$	~450 (IR)[b]		319 (IR)

[a] IR samples were Nujol mulls; Raman samples were enclosed in capillaries and excited by the 5682-Å line of a Kr laser. Similar results were obtained for the P-*i*-Pr_3 analogues. [b] Partially obscured. ν(HH) was relatively clear in the $P(C_6D_{11})_3$ analogue.

0.84 Å (neutron, ΔF), slightly larger than that obtained from free H_2 (0.74 Å). The H_2 ligand axis is approximately parallel to the trans phosphorous–phosphorous direction.

Vibrational spectra of solid samples of the H_2, D_2, and HD forms (M = W) are consistent with coordination of molecular H_2. Of the six fundamentals expected from η^2 $M-H_2$ binding, four are observed (Table I). Bands at 950 and 1570 cm^{-1} have been assigned as symmetric and asymmetric $M-H_2$ stretches, respectively. Both modes exhibit deuterium isotopic shifts close to those predicted for pure $M-H_2$ stretching symmetry coordinates. Most importantly, an entirely new set of band positions is observed for the HD complexes, intermediate to those of the H_2 and D_2 species.[10] The H–H stretch is observed at 2690 cm^{-1} in the Nujol mull IR spectrum of $W(CO)_3(PCy_3)_2(H_2)$, while the HD species exhibits a similar broad IR absorption at ca. 2360 cm^{-1}, which we attribute to the H–D stretch. Although the D–D IR stretch was obscured for the D_2 complex, Raman spectra show a weak, broad feature at ca. 1900 cm^{-1}, which we assign to this mode intensified by coupling with the nearby C–O stretches.[11] The deformation and torsional modes of the metal-bound H_2 are more difficult to assign as they are weak or unobserved. However, an IR feature at 319 cm^{-1} for $W(CO)_3(PCy_3)_2(D_2)$ and absent at this frequency for the H_2 species is attributed to an $M-D_2$ deformation. Also, we note that frequencies of several Raman modes in the 400–600-cm^{-1} region, where M–CO stretch and M–C–O deformations occur, are significantly shifted by deuterium substitution. Three of these modes, including the strongest at 452 cm^{-1}, shift to higher frequency (e.g., 456 cm^{-1}) upon deuteration. We ascribe these unusual deuterium shifts to the presence of $M-H_2$ deformation modes strongly coupled to the M–CO stretch and M–C–O deformation and stress that metal hydride complexes do not exhibit bands in these low-frequency regions.[12]

The ^1H NMR spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ under H_2 atmosphere shows a single, broad, temperature- and concentration-independent resonance due to the H_2 ligand at τ 14.21.[13] No coupling to ^{31}P or ^{183}W is resolved in the temperature range +60 to −85 °C. The broad line width (15–40 Hz at half-height) over such a large range may result from exchange and fluxionality involving the H_2 ligand and/or dipolar interaction between the two closely separated hydrogen atoms. The chemical shift is comparable to that found for the hydride ligands in $WH_4(PEt_3)_4$.[14] Unequivocal evidence for direct H–H bonding is provided by the ^1H spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$,[15] which shows splitting of the signal at τ 14.2 by spin 1 deuterium into a 1:1:1 triplet with J_{HD} = 33.5 Hz. This value is an order of magnitude larger than that found for compounds containing nonbonded H and D atoms and can be compared to that for HD gas, 43.2 Hz.[16] Since the observed coupling does not vary significantly with the amount of excess HD present, we conclude that it indeed represents J_{HD} for the coordinated HD and reflects a decreased H–D bond order relative to free HD. The line width of the HD resonances is considerably less broad (8 Hz at 35 °C) than that for the H_2 signal (24 Hz), consistent with reduced dipolar broadening. $^{31}P\{^1H\}$ NMR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ shows a single resonance with ^{183}W satellites.[13] No coupling to the H_2 protons is resolved at 35 °C in the ^{31}P spectrum.

The H_2 complexes are significant in that they may represent an arrested form of oxidative addition of H_2 to metals. Low-temperature neutron diffraction experiments, using continuous as well as pulsed sources, are currently under way to obtain more meaningful structural parameters and will be the subject of future publications.

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Registry No. $Mo(CO)_3(PCy_3)_2$, 73690-53-6; $W(CO)_3(PCy_3)_2$, 73690-56-9; *mer-trans*-$Mo(CO)_3(PCy_3)_2(H_2)$, 88211-52-3; *mer-trans*-$W(CO)_3(PCy_3)_2(H_2)$, 88211-53-4; $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$, 88211-54-5; $W(CO)_3(p\text{-}i\text{-}Pr_3)_2(H_2)$, 88211-55-6; $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2$, 88211-56-7; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$, 88211-57-8.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, least-squares planes, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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(10) In conrast, see: Eberhardt, G. G.; Vaska, L. *J. Catal.* **1967**, *8*, 183.

(11) ν_{CO} = 1962.3, 1857.0 cm^{-1} for $W(CO)_3(PCy_3)_2(H_2)$; 1962.8, 1847.0 cm^{-1} for the D_2 species.

(12) For metal hydride complexes, δ_{MH} generally occurs in the region 700–900 cm^{-1}. Rare-gas matrix-isolated hydrides of the type FeH_2 have recently been described (Ozin, G. A.; McCaffrey, J. G.; McIntosh, D. F. *J. Pure Appl. Chem.*, in press) and found to exhibit IR bands in the 300–400-cm^{-1} region. Preliminary inelastic neutron scattering studies of $W(CO)_3(PCy_3)_2(H_2)$ indicate the presence of $M-H_2$ modes in the 300–550-cm^{-1} region (Eckert, J.; Swanson, B. I.; Kubas, G. J., unpublished results).

(13) ^1H NMR ($C_6D_5CD_3$, 90 MHz) τ 7.88 (m, J_{HH} = 6.9 Hz), 8.86 (m, J_{HH} = 6.5 Hz), 14.21 (s); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 121.5 MHz) δ 33.6 (s, J_{PW} = 273.7 Hz).

(14) Meakin, P.; Gugenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.

(15) Prepared from 98% HD purchased from MSD Isotopes, Montreal, Canada.

(16) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.

N-Fluoro-*N*-alkylsulfonamides: Useful Reagents for the Fluorination of Carbanions

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While the introduction of fluorine into organic molecules is of broad interest,[1] being used extensively in physical, theoretical, and mechanistic studies and to alter the activity of biomolecules, methodology for the fluorination of carbanions remains limited. Perchloryl fluoride,[2] while an effective reagent for this purpose, is a toxic gas with a tendency to form explosive product mixtures. *N*-fluoroperfluoropiperdine[3] is known to effect anion fluorinations but is very difficult to prepare.[4] Very recently it was shown that treatment of malonate anions with *N*-fluoropyridone[5] affords the corresponding fluorinated derivatives. However, reported yields were low and the scope of the reaction appears to be limited.

We wish to report that *N*-fluoro-*N*-alkylsulfonamides are ef-

Table I. Preparation of *N*-Fluoro-*N*-alkylsulfonamides, RSO_2NFR'

compd[8]	R	R'	F_2, %	yield,[a] %	^{19}F NMR[b]
1	*p*-tolyl	methyl	1	59	−37.62
2	*p*-tolyl	*tert*-butyl	5	14	−62.78
3	*p*-tolyl	*exo*-2-norbornyl	1	47	−46.91
4	*p*-tolyl	*endo*-2-norbornyl	1	71	−36.98
5	*p*-tolyl	cyclohexyl	5	11	−71.63
6	*p*-tolyl	neopentyl	5	57	−36.88
7	*n*-butyl	neopentyl	1	50	−38.40

[a] Products isolated by column chromatography on silica. [b] Upfield from $CFCl_3$.

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