Synthesis and Structure of $HW_2(CO)_9(NO)$

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Summary $HW_2(CO)_9NO$ has been prepared by the reaction of $[HW_2(CO)_{10}]^-$ with $NaNO_2$–acetic acid and has been found by *X*-ray crystallography to have a distorted D_{4d} conformation with a bent W–**H**–W bond.

WHILE a large variety of transition metal hydrides is known,[1] only a few nitrosyl hydrides have been prepared.[2] In this study, treatment of $[HW_2(CO)_{10}]^-$ with $NaNO_2$–HOAc yielded $HW_2(CO)_9(NO)$.† Conclusive evidence for the hydrogen is provided by the n.m.r. spectrum which showed a singlet‡ at τ 21·77 in acetone. Absorptions in the 800—1200 cm^{-1} region of the Raman suggested a bridging position for the hydrogen.[3]

Crystal data: Space group $P\bar{1}$ (triclinic): $a = 12{\cdot}24(1)$, $b = 9{\cdot}64(1)$, $c = 6{\cdot}93(1)$ Å, $\alpha = 112{\cdot}8(1)$, $\beta = 91{\cdot}3(1)$, $\gamma = 97{\cdot}4(1)$, $U = 744{\cdot}6$ Å^3, $Z = 2$, $D_m = 2{\cdot}92$ g/cm^3, $D_c = 2{\cdot}90$ g/cm^3. One hemisphere of data was collected on an automated Nonius CAD-3 diffractometer up to a limit of 50° in 2θ (Mo-K_α radiation) and corrected for absorption effects to give 1932 reflections of intensity greater than 3σ. The structure was solved by standard procedures using a carbon atom in place of the nitrogen atom and refined to a current

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† Satisfactory elemental analysis and mass and i.r. spectra were obtained; i.r. spectrum (cyclohexane): 2069m, 2045s, 2011w, 1989w, 1953sh, 1944s, 1735br,m, and 1717sh cm^{-1}.

‡ Limited solubility prevented the observation of ^{183}W satellites.

R factor of 6·1%. Preliminary evidence§ suggests an axial position for the nitrogen atom.

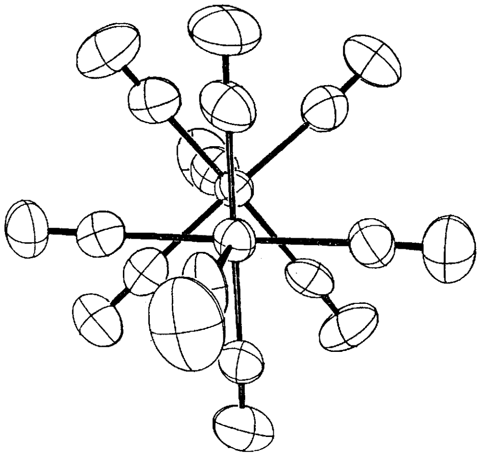

FIGURE. *Molecular geometry of* $HW_2(CO)_9(NO)$ *showing all non-hydrogen atoms.*

The geometry of the molecule is shown in the Figure. The molecule exhibits a distorted D_{4d} symmetry, with the equatorial carbonyls in a staggered configuration such that the planes defined by the equatorial $W(CO)_4$ groups are at an angle of 29°, as compared with 16° in $HRe_2Mn(CO)_{14}$[4] and 21° in $HRe_3(CO)_{14}$.[5]

While the hydrogen atom could not be crystallographically located, the long W–W distance (3·329 Å)¶ and the octahedral co-ordination about the tungsten atoms strongly support a bridging position for the hydrogen. The W–H–W angle can be estimated to be 159° by defining the hydrogen position as the intersection of the two W–CO(axial) lines. While many structures containing bent M–H–M bonds have been postulated, the bend is usually necessitated by the geometry of the molecule, as in $H_3Mn_3(CO)_{12}$[6] and $HMn_2(CO)_8[P(C_6H_5)_2]$.[7] In a few cases, such as $HRe_2Mn(CO)_{14}$, $HRe_3(CO)_{14}$, and the present compound, there does not seem to be any obvious reason why this should be so. However, compounds containing bent M^1–H–M^2 linkages seem to occur whenever M^1 and M^2 are in different chemical environments. When M^1 and M^2 are equivalent, as in $[HCr_2(CO)_{10}]^-$,[8] the M^1–H–M^2 linkage is linear.

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§ Equatorial W–C distances are 2·05 Å; axial W–C distances are 1·90 Å.

¶ The covalent radius of W was taken to be 1·56 Å.[8,9]

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