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Heterometallic species containing Cp_2MH_2 (M = Mo and W) and Cu^+ or Ag^+ are inner sphere redox intermediates

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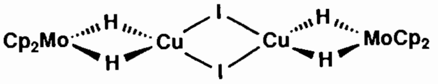
Abstract

Reaction of $Cu(NCMe)_4^+$ with Cp_2MH_2 (M = Mo or W) in a 1:2 mole ratio yields $(Cp_2MH_2)_2Cu^+$, as the PF_6^- salt. IR and ^1H NMR data are consistent with a structure in which all hydrides are bridging M to copper. An X-ray diffraction structure determination of the compound with M = Mo confirms this conclusion; the unit cell contains two crystallographically-independent cations with significantly different CuH_4 coordination geometries: the MoH_2 planes have dihedral angles of 31.1 and 51.0°. Crystallographic data (at −157 °C): $a = 20.263(6)$, $b = 10.434(2)$, $c = 21.109(6)$ Å, $Z = 8$ in space group *Pbnb*. Additional $Cu(NCMe)_4^+$ has no effect on $(Cp_2WH_2)_2Cu^+$. Reaction of Cp_2WH_2 with $AgBF_4$ gives first $(Cp_2WH_2)_2Ag^+$, which shows Ag/hydride coupling in the ^1H NMR spectrum at −75 °C. Additional Ag^+ in MeCN gives oxidation to equimolar $Cp_2W^{VI}H_3^+$ and $Cp_2W^{IV}H(NCMe)^+$, via the adduct $(Cp_2WH_2Ag)_2^{2+}$, whose IR spectrum is consistent with μ_3-hydrides. While$(Cp_2WH_2)_2Ag^+$ is not oxidized by $Cu(NCMe)_4^+$, $(Cp_2WH_2)_2Cu^+$ is completely oxidized by Ag^+, suggesting that the aggregate $(Cp_2WH_2MM')_2^{2+}$ has inequivalent sites for M and M′, and thus two isomeric forms.

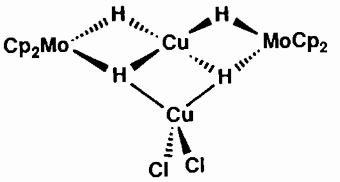
Introduction

We have been studying the chemical oxidation of polyhydrides of the second- and third-row transition metals as one means of increasing their reactivity [1–4]. One of the oxidants (or oxidant-mimics) we have employed is $[Cu(NCMe)_4]PF_6$, which allows isolation of adducts which we believe to be pertinent to inner sphere oxidations not only with cuprous ion, but also with Ag^+. These adducts have been shown to involve multiple hydride bridging [3] ($CuRe_2H_{10}(PMePh_2)_6^+$) and unexpected aggregation [2] ($Cu_2Re_4H_{16}(PMe_2Ph_4)_8^{2+}$), and thus the Cu^+ electrophile also serves as a versatile building block for the synthesis of mixed-metal clusters.

Following the discovery [3] that a triple μ_2-H linkage is possible to Cu^+ (in $P_3H_2Re(\mu\text{-}H)_3Cu(\mu\text{-}H)_3ReH_2P_3^+$, P = PMe_2Ph), we examined hydrides where more conventional patterns of bonding (i.e. a Cu^+ coordination number of four) and structure (tetrahedral Cu^+) were possible. The dihydrides Cp_2MH_2 (M = Mo, W) were attractive to us in this regard and indeed the group of Bulychev [5a] has structurally characterized a 1:1 adduct of empirical formula $Cp_2MoH_2 \cdot CuI$. This is in fact a dimer, A, with structure $Cp_2Mo(\mu\text{-}H)_2Cu(\mu\text{-}I)_2Cu(\mu\text{-}H)_2MoCp_2$, where each copper achieves tetrahedral coordination. (Cp_2MoH_2 shows a *cis*-dihydride moiety [5b]). More recently, the group in Moscow [5a] has shown that the chloride derivative of the above compound is in no way analogous (see **B**), but instead contains inequivalent Cu^+ centers, one copper having two Cp_2MoH_2 units bound to it. The tetrahydride coordination sphere around this copper is rotated only ~17° from being planar, and is devoid of chloride. Two of the four hydride ligands in this unit donate additionally to a non-linear $CuCl_2$ unit to give an aggregate of net zero charge. This second copper thereby achieves tetrahedral H_2Cl_2 coordination.



A



B

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In view of the preference of four-coordinate Cu^+ to be tetrahedral when coordinated to conventional Lewis bases, we were intrigued by the approximately planar four coordination found [6] around one copper in $(Cp_2MoH_2CuCl)_2$. If the molecule is dissected into $Cp_2Mo(\mu\text{-}H)_2Cu(\mu\text{-}H)_2MoCp_2^+$ and $CuCl_2^-$, it is possible that $Cp_2Mo(\mu\text{-}H)_2Cu(\mu\text{-}H)_2MoCp_2^+$ might indeed contain tetrahedral copper, but that this twists towards planarity in response to functioning as a bidentate ligand towards $CuCl_2^-$. We describe here the successful synthesis and characterization of $(Cp_2MH_2)_2Cu^+$, M = Mo and W, and the surprising resolution of the question of the preferred geometry at copper in this cation.

Experimental

General procedures

All operations were carried out under prepurified nitrogen with solvents dried and deoxygenated by using conventional procedures. IR spectra were recorded on a Perkin-Elmer 283 spectrometer and calibrated by using polystyrene film. Proton NMR spectra were recorded on Varian HR-220 and Nicolet NT-360 spectrometers. Photolysis employed a Hanovia 450 W medium-pressure mercury lamp and Pyrex glassware. The hydrides Cp_2MH_2 were synthesized using published procedures [7, 8].

$[\{Cp_2MoH_2\}_2Cu]PF_6$ (1)

In a typical experiment, solid $Cu(MeCN)_4PF_6$ [9] (0.041 g, 0.12 mmol) was added via an addition tube to a cooled (dry ice-isopropanol bath) yellow THF (5 ml) solution of Cp_2MoH_2 (0.05 g, 0.22 mmol). The yellow slurry was stirred for 1 h at low temperature. The reaction mixture was then allowed to warm to room temperature. The yellow precipitate was filtered, washed with THF (2×3 ml) and dried *in vacuo*. IR (nujol, cm^{-1}): ν(Mo–H–Cu), 1625(m, br), ν(P–F), 850(vs), 563(s). ^1H NMR (CD_3CN): $\delta + 4.77$ (s, 5H), -10.75 (s, 1H).

$[\{Cp_2WH_2\}_2Cu]PF_6$ (2)

Compound **2** was synthesized from Cp_2WH_2 (0.03 g, 0.095 mmol) and $Cu(MeCN)_4PF_6$ (0.018 g, 0.048 mmol) in a manner analogous to that for compound **1**. IR (nujol): ν(W–H–Cu), 1720(br, m) and 1624(m); ν(P–F), 855(s). ^1H NMR (CD_3CN): $\delta + 4.9$ (s, 5H), -13.6 (s with satellites, J(WH) = 80 Hz, 1H).

$[(Cp_2WH_2)_2Ag]BF_4$ (3)

This compound was synthesized by addition of solid $AgBF_4$ (0.0092 g, 0.048 mmol) to a yellow frozen (−78 °C) CH_3CN solution of Cp_2WH_2 (0.03 g, 0.095 mmol), followed by warming to 25 °C. The resulting yellow solution showed (^1H NMR) quantitative conversion to $(Cp_2WH_2)_2Ag^+$. ^1H NMR (CD_3CN, 16 °C): 4.87 (s, 5H); -12.5 (s, 1H, J(WH) = 73 Hz) ν(MH) (in CH_3CN) = 1778(br).

Silver oxidation of Cp_2WH_2

Solid $AgBF_4$ (0.018g, 0.093 mmol) was added to a frozen CH_3CN solution of Cp_2WH_2 (0.030 g, 0.095 mmol), followed by warming to 25 °C. Black Ag^0 precipitated immediately and was removed by filtration. The resulting yellow filtrate showed quantitative (^1H NMR) conversion to $Cp_2WH(NCMe)^+$ and $Cp_2WH_3^+$. For spectral data, see below.

$(Cp_2WH_2Ag)_2(BF_4)_2$

Solid $AgBF_4$ was added to a cooled (−78 °C) THF solution of Cp_2WH_2 (1:1 mole ratio). The solution was allowed to warm slowly to 25 °C, yielding a brown precipitate which was isolated by filtration. This solid is insoluble in all spectroscopic solvents examined, except for acetonitrile, in which it reacts as described above.

$AgBF_4$ oxidation of $[(Cp_2WH_2)_2Cu]PF_6$

Solid $AgBF_4$ (0.009 g, 0.046 mmol) was added to a CD_3CN solution of $[(Cp_2WH_2)_2Cu]PF_6$ (0.039 g, 0.046 mmol). A black metallic precipitate formed immediately. The surpernatant solution showed (^1H NMR) quantitative conversion to equimolar $Cp_2WH(NCMe)^+$ and $Cp_2WH_3^+$. For $[Cp_2WH(MeCN)]^3$: ^1H NMR (CD_3CN, 16 °C): 5.18 (s, 10H), 2.39 (s, 3H), -12.8 (s, 1H, J(WH) = 69 Hz). ν(MH) in Nujol: 1768w. For $[Cp_2WH_3]^+$: ^1H NMR (CD_3CN, 16 °C): $+5.57$ (s, 10H), -6.14 (t, 1H, J(HH) = 7.9 Hz, J(WH) = 47 Hz), -6.46 (d, 2H, J(HH) = 7.9 Hz, J(WH) = 69 Hz).

Attempted oxidation of $[(Cp_2WH_2)_2Ag]BF_4$ by Cu^+

The above procedure was repeated using $Cu(MeCN)_4PF_6$ (0.018 g, 0.04 mmol) and $[(Cp_2WH_2)_2Ag]BF_4$ (0.039 g, 0.047 mmol). The ^1H NMR spectrum of the resulting solution revealed only unreacted $[(Cp_2WH_2)_2Ag]BF_4$ and $Cu(MeCN)_4PF_6$.

X-ray diffraction study of $[Cu(H_2MoCp_2)_2]PF_6 \cdot H_2O$

Under a nitrogen atmosphere, a small fragment of a needle-shaped crystal, grown by vapor diffusion of Et_2O into an acetone solution, was attached to a glass fiber using silicone grease, transferred to a goniostat, and cooled to −157 °C for all measurements [10]. A systematic search of a limited hemisphere of reciprocal space revealed an orthorhombic lattice with extinctions corresponding to the unique centrosymmetric space group *Pbnb* (and alternate setting of *Pccn*, No. 56, equivalent positions are $\pm x, y, z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$; $\frac{1}{2}+x,$

TABLE 1. Crystal data for $[Cu(H_2MoCp_2)_2]PF_6 \cdot H_2O$

Formula	$C_{20}H_{26}OF_6PCuMo_2$
Color	yellow
Crystal dimensions (mm)	0.12×0.11×0.11
Space group	*Pbnb*
Cell dimensions (at −157 °C; 30 reflections)	
a (Å)	20.263(6)
b (Å)	10.434(2)
c (Å)	21.109(6)
Molecules/cell	8
Volume	4462.74
Calculated density (gm/cm^3)	2.03
Wavelength (Å)	0.71069
Molecular weight	682.8
Linear absorption coefficient (cm^{-1})	21.6
No. unique intensities	2937
No. with $F > 3.00\sigma(F)$	2235
$R(F)$	0.0380
$R_w(F)$	0.0409
Goodness of fit for the last cycle	0.807
Maximum Δ/σ for last cycle	0.05

$-y, \frac{1}{2}+z$; *and* $-x, \frac{1}{2}-y, \frac{1}{2}+z$), see Table 1. The structure was readily solved by direct methods (MULTAN78) and Fourier techniques. Two independent cations were located in the asymmetric unit, with the copper of each lying on a crystallographic two-fold axis; also located were one PF_6^- anion and one water molecule. All hydrogen atoms were located and refined with the exception of the two hydrogens associated with the water solvent molecule. The water oxygen lies between 3.0 and 3.2 Å from four fluorine atoms in the cell. A psi scan of several reflections was essentially flat, so no absorption correction was performed. The results of the structure study appear in Tables 1–4 and Figs. 1 and 2.

The PF_6^- ion is unexceptional, with a mean P–F distance of 1.572(17) Å and all *cis* angles within 2.2° and 90°. Carbons of the cyclopentadienyl rings are within 1σ of their least-squares plane, and the hydrogens are within $\pm 1\sigma$ of the five-carbon planes. The mean of the twenty C–C distances is 1.403(16) Å. Carbon–hydrogen distances average 0.86 Å, ranging from 0.75(10) to 1.01(9) Å. The ring least-squares planes make angles of 87.5, 87.5, 87.0 and 87.0° with lines from Mo to the ring centroids.

Results

Reactions of Cp_2MH_2 with Cu(I)

It was thought that the presence of a *cisoid* arrangement of two or more hydride ligands was conducive to the formation of the sort of pre-redox intermediates previously detected. Consequently, in searching for a d^2 substrate containing Mo or W, the Cp_2MH_2 species appeared attractive [5b]. The reaction of $Cu(MeCN)_4PF_6$ with Cp_2MoH_2 in THF in a 1:2 mole ratio (suggested by our results with ReH_5P_3) permits the isolation of the adduct $[(Cp_2MoH_2)_2Cu]PF_6$ (**1**). This product stoichiometry was suggested initially since the 1:2 reaction gives no other product, and consumes all of each reagent. The ^1H NMR in CD_3CN shows only one Cp resonance, and only one hydride resonance. The IR spectrum of this yellow solid product shows a broad medium intensity band at 1625 cm^{-1}, consistent with a bridging hydride motion (for Cp_2MoH_2, $\nu(MoH) = 1850$ cm^{-1}). The tungsten analog of **1** was also isolated, and displayed similar spectroscopic features. This adduct also exhibits W–H coupling, and the

TABLE 2. Fractional coordinates and isotropic thermal parameters[a] for $[Cu(H_2MoCp_2)_2]PF_6 \cdot H_2O$

	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$	$10 \times B_{iso}$[b]
Cu	7500*	1843(2)	7500*	21
Mo	8459.0(3)	1759(1)	6662.4(3)	13
C(3)	9412(4)	2274(9)	7156(4)	20
C(4)	9550(4)	1353(8)	6701(4)	19
C(5)	9014(4)	1702(9)	7621(4)	21
C(6)	8893(4)	438(9)	7452(5)	24
C(7)	9224(4)	197(9)	6875(4)	23
C(8)	8448(5)	3249(10)	5877(4)	32
C(9)	7774(5)	3038(11)	6042(5)	30
C(10)	7620(4)	1774(10)	5907(4)	25
C(11)	8181(5)	1162(10)	5655(4)	25
C(12)	8676(5)	2090(11)	5630(4)	31
Cu′	2500*	188(1)	7500*	19
Mo′	3388.1(3)	135(1)	6589.5(3)	12
C(3)′	4462(4)	344(9)	6917(4)	20
C(4)′	4420(4)	−595(9)	6420(4)	21
C(5)′	4032(4)	−1642(8)	6633(4)	22
C(6)′	3867(4)	−1383(9)	7261(5)	24
C(7)′	4124(4)	−169(9)	7431(4)	21
C(8)′	2984(5)	−97(11)	5598(4)	23
C(9)′	2466(5)	464(9)	5937(4)	26
C(10)′	2690(5)	1663(9)	6144(4)	26
C(11)′	3333(5)	1850(9)	5918(4)	29
C(12)′	3503(5)	755(10)	5580(4)	25
P(1)	608(1)	2534(2)	4587(1)	21
F(2)	88(3)	2479(6)	4021(3)	44
F(3)	414(4)	1108(7)	4746(4)	76
F(4)	1161(3)	2025(7)	4127(3)	55
F(5)	1125(4)	2558(8)	5142(3)	57
F(6)	819(4)	3932(6)	4395(5)	71
F(7)	65(4)	3056(11)	5028(5)	105
O(1)	9158(3)	5120(7)	930(3)	42(2)
H(1)	694(3)	270(6)	785(3)	7(14)
H(2)	719(4)	86(7)	798(3)	28(18)
H(1)′	279(4)	−75(9)	691(4)	47(24)
H(2)′	318(4)	109(9)	714(4)	49(24)

Parameters marked by an asterisk (*) are fixed by symmetry. Parameters marked by a prime are in cation B; the others are in cation A. [a]Fractional coordinates are $\times 10^3$ for hydrogen atoms. [b]Isotropic values for those atoms refined anisotropically are calculated using the formula given in ref. 11.

TABLE 3. Bond distances (A) for $[Cu(H_2MoCp_2)_2]PF_6 \cdot H_2O$

	Molecule A	Molecule B
Mo–Cu	2.6287(9)	2.6335(8)
Mo–C(3)	2.259(8)	2.294(8)
Mo–C(4)	2.253(8)	2.255(8)
Mo–C(5)	2.317(8)	2.269(8)
Mo–C(6)	2.335(9)	2.336(8)
Mo–C(7)	2.293(8)	2.341(8)
Mo–C(8)	2.272(9)	2.261(8)
Mo–C(9)	2.329(10)	2.346(8)
Mo–C(10)	2.330(8)	2.330(9)
Mo–C(11)	2.286(8)	2.284(9)
Mo–C(12)	2.250(9)	2.238(9)
Mo–H(1)	1.63(7)	1.66(9)
Mo–H(2)	1.79(7)	1.59(9)
Cu–H(1)	1.62(6)	1.70(9)
Cu–H(2)	1.56(7)	1.83(9)
Mo–Ct(1)[a]	1.956	1.961
Mo–Ct(2)	1.959	1.962

[a] Ct(i) represents the centroid of the Cp ligands.

TABLE 4. Bond angles (°) for $[Cu(H_2MoCp_2)_2]PF_6 \cdot H_2O$

	Molecule A	Molecule B
Mo–Cu–Mo*	176.17(8)	177.60(7)
Cu–Mo–H(1)	36.1(22)	39(3)
Cu–Mo–H(2)	35.4(24)	43(3)
H(1)–Mo–Ct(1)	103.7	101.7
H(1)–Mo–Ct(2)	103.9	105.5
H(2)–Mo–Ct(1)	101.2	102.6
H(2)–Mo–Ct(2)	106.3	103.1
Ct(1)–Mo–Ct(2)	145.9	144.7
Ct(1)–Mo–Cu	103.3	107.4
Ct(2)–Mo–Cu	110.8	107.8
H(1)–Mo–H(2)	71(3)	82(4)
Mo–Cu–H(1)*	147(3)	140(4)
Mo–Cu–H(2)*	135(3)	146(3)
Mo–Cu–H(1)	36.3(23)	38(3)
Mo–Cu–H(2)	41.5(27)	36(3)
H(1)–Cu–H(1)*	113(5)	109(6)
H(1)–Cu–H(2)	78(3)	74(4)
H(2)–Cu–H(2)*	98(5)	118(6)
Mo–H(1)–Cu	108(4)	103(5)
Mo–H(2)–Cu	103(4)	100(5)

An asterisk indicates an atom related by the C_2 axis of symmetry.

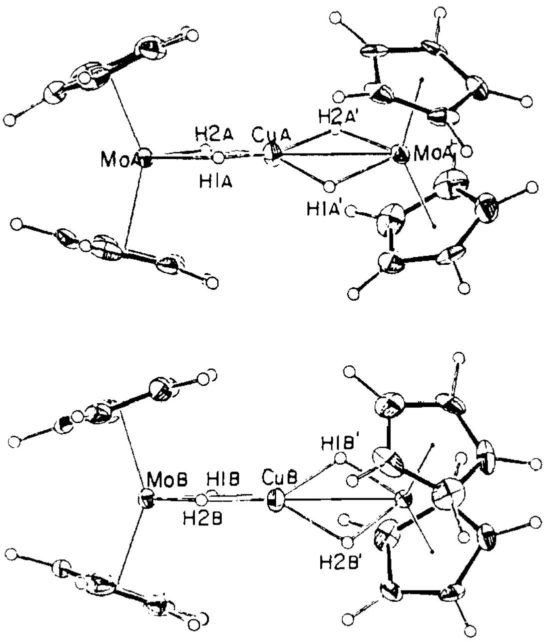

Fig. 1. ORTEP drawings of the two crystallographically-independent $(Cp_2MoH_2)_2Cu^+$ ions in the PF_6^- salt. The crystallographic C_2 axis passes through each copper, relating right and left (primed) sides of the molecule.

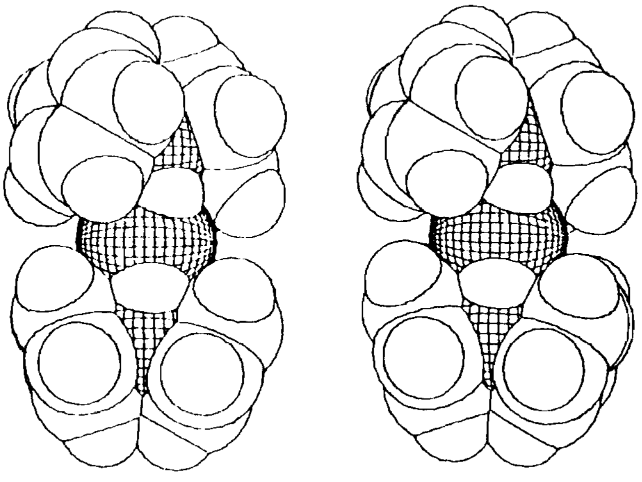

Fig. 2. Stereo space-filling drawing of cation B of $(Cp_2MoH_2)_2Cu^+$. The C_2 axis is perpendicular to the page, passing through copper.

coupling constant (80 Hz) actually exceeds that of Cp_2WH_2 (75 Hz). The intensity of each ^{183}W satellite, about 8% of the central peak, indicates that the hydrides do *not* migrate rapidly between the two tungsten nuclei, but remain associated with only one W. The IR spectrum of this adduct shows only a bridging hydride stretching band; no terminal hydrides are evident. These reactions are thus summarized by eqn. (1).

$$2Cp_2MH_2 + [Cu(MeCN)_4]PF_6 \xrightarrow{THF} [(Cp_2MH_2)_2Cu]PF_6 + 4MeCN \quad (1)$$

Structure Determination of $[(Cp_2MoH_2)_2Cu]PF_6 \cdot H_2O$

The unit cell is composed of eight water molecules and PF_6^- ions in general positions and four each of two crystallographically-independent $Cu(H_2MoCp_2)_2{}^+$ cations. Each of these independent cations (Fig. 1) has a crystallographic C_2 axis which passes through only the copper atom. Although not required by symmetry, the Mo–Cu–Mo units are linear (176.2 and 177.6°). In general, except for the relative rotational conformations of the two Cp_2Mo ends of the independent cations, these two cations show exceptional consistency in distances and angles. Ring–centroid/Mo/ring–centroid angles are 145.9 and 144.7°. In each cation, Mo, Cu and the two ring centroids are co-planar to within 0.003 Å. These planes intersect the Mo–(μ-H)$_2$–Cu planes at angles of 88.0 and 88.7°. Thus, the two hydride and the copper atoms lie accurately in the idealized mirror plane which relates the two cyclopentadienyl rings.

All hydrogens in both cations were refined. The four independently determined Mo–H distances average 1.67(4) Å, and the four independent Cu–H distances average 1.68(6) Å. The X-ray diffraction study thus shows unequivocally that all hydrides are bridging, which confirms the IR spectral data. The major difference between the two crystallographically-independent cations lies in the rotation of one (ring-centroid)$_2$Mo plane relative to that at the other end of the same cation (Fig. 1). These dihedral angles are 35.3 and 53.7°. Since this orientation directs the MoH_2 planes, the distinction between the two cations lies in the tetrahydride coordination geometry about copper. The angle between the two Mo(μ-H)$_2$Cu planes (which are planar to within ± 0.3 Å) in the cations are 31.1 and 51.0°. Each of these angles deviates markedly from the typical (tetrahedral) interplanar angle for four-coordinate Cu(I) (90°), and is additionally noteworthy because the two angles are so different in the same unit cell. One cation is closer to planar, the other to tetrahedral. The Cu–Mo distance does not differ in the two cations. Examination of a space-filling model (Fig. 2) shows that these variations in rotational conformation are not dictated by end-to-end Cp/Cp repulsions.

Solution behavior of $(Cp_2WH_2)_2Cu^+$

Attempts to elicit redox chemistry from $(Cp_2WH_2)_2Cu^+$, either by heating or irradiation, were unsuccessful. Since the stoichiometry of this compound deviates from both one- and two-electron oxidation, the reaction of this monocationic adduct with an additional mole of $Cu(MeCN)_4PF_6$ was investigated. When combined in CD_3CN, there is neither gas evolution nor precipitation of Cu^0. The ^{1}H NMR spectrum of this solution differs from that of a solution of $(Cp_2WH_2)_2Cu^+$ only in a shift of the hydride resonance by 0.17 ppm further upfield. A resonance due to uncoordinated MeCN is also detected*. The IR spectrum of the solid formed on vacuum removal of CD_3CN has the features of a simple mixture of $[(Cp_2WH_2)_2Cu]PF_6$ and $Cu(MeCN)_4PF_6$. Thus, although neither oxidation nor formation of any new adduct takes place, the shift of the hydride resonance is indicative of a shift in the following dissociative equilibrium (acetonitrile solvent),

$$2Cp_2WH_2 + Cu(MeCN)_4^+ \overset{MeCN}{\rightleftarrows} (Cp_2WH_2)_2Cu^+ + 4MeCN \qquad (2)$$

which is displaced to the right when excess $Cu(MeCN)_4^+$ is added. Heating a 1:1 mixture of $[(Cp_2WH_2)_2Cu]PF_6$ and $Cu(MeCN)_4PF_6$ in CD_3CN at 65 °C (or photolysis) for several hours results in no consumption of these reagents.

Reactions of Cp_2WH_2 with $AgBF_4$

Having established that $Cu(MeCN)_4PF_6$ is unable to oxidize Cp_2WH_2, we turned to the stronger oxidant Ag^+. Reaction of $AgBF_4$ with Cp_2WH_2 (1:2 mole ratio) in THF permits isolation of a dark brown solid product, stable at 25 °C, with no deposition of Ag^0. This solid, dissolved in CD_3CN at 16 °C, shows one Cp and one hydride ^{1}H NMR resonance. The hydride resonance shows tungsten satellites ($J(WH) = 73$ Hz), and the IR spectrum has a bridging hydride stretch at 1770 cm^{-1} (for Cp_2WH_2, $\nu(WH) = 1912$ cm^{-1}). At -75 °C, in d_6-acetone, the hydride resonance of a freshly prepared solution, is split into a doublet due to coupling to ^{109}Ag and ^{107}Ag (the separate doublets for each isotope are not resolved**. Upon warming of this solution to -20 °C, the doublet coalesces to a broad singlet, which sharpens further by 25 °C. These phenomena are consistent with the following rapid equilibrium (eqn. (3), S = solvent), although displaced far to the left at NMR concentrations; no Cp_2WH_2 is evident by IR spectroscopy in CH_3CN at 25 °C.

$$\underset{\mathbf{3}}{(Cp_2WH_2)_2Ag^+} \overset{S}{\rightleftarrows} Cp_2WH_2AgS_n^+ + Cp_2WH_2 \qquad (3)$$

Solutions of $[(Cp_2WH_2)_2Ag]BF_4$ in CD_3CN are stable at 25 °C for at least 48 h. However, CH_3CN solutions react rapidly upon addition of equimolar $AgBF_4$ to deposit Ag^0 and leave a yellow–brown solution. Assay (^{1}H NMR) of this solution within 3 h shows two products, in a 1:1 stoichiometry. One product is readily identified by its ^{1}H NMR intensities and by comparison to an authentic sample [13] as $Cp_2WH_3^+$. The identity of this product was further confirmed by its conversion to Cp_2WH_2 on addition of excess NEt_3. The second product was characterized as the BF_4^- salt of the

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*In CD_3CN, the acetonitriles of $Cu(MeCN)_4PF_6$ exchange immediately with free CD_3CN. The resonance of CH_3CN thus appears at the resonance for free CH_3CN in the ^{1}H NMR.

**Both isotopomers are spin active ($I = \frac{1}{2}$) and are almost equally abundant (^{107}Ag, 51%; ^{109}Ag, 49%). However, the gyromagnetic ratios are similar ($\gamma^{107}Ag/\gamma^{109}Ag = 0.87$) for both isotopomers, which is probably the reason for the unresolved isotopic couplings [12a]. Similar behavior has been noted by other researchers [12b].

previously unreported cation $Cp_2WH(MeCN)^+$. It exhibits three ^1H NMR singlets. The tungsten-bound MeCN does not exchange with CD_3CN solvent over a period of 1 h. This compound, isolated as a brown oil, has a W–H stretching frequency at 1775 cm^{-1}. The consequences of Ag(I) oxidation of Cp_2WH_2 are summarized in eqn. (4).

$$2Cp_2WH_2 + Ag^+ \longrightarrow (Cp_2WH_2)_2Ag^+ \xrightarrow[MeCN]{Ag^+} \underset{\mathbf{4}}{Cp_2WH_3^+} + \underset{\mathbf{5}}{Cp_2WH(MeCN)^+} + 2Ag^0 \quad (4)$$

If the second equivalent of Ag^+ in eqn. (4) is delivered in THF rather than acetonitrile solvent, a dark brown solid precipitates. The IR spectrum of this compound, with its lowered hydride stretching frequencies (1760 and 1550 cm^{-1}), suggests the presence of μ_3-hydride ligands in a cation of stoichiometry $[Cp_2WH_2Ag(solvent)_n]_2^{2+}$. The insolubility of this salt in THF, CH_2Cl_2 and acetone, while preventing its examination by NMR, provides assurance that this is not simply $[(Cp_2WH_2)_2Ag]BF_4$ or monomeric $Cp_2WH_2Ag(solvent)^+$ (see eqn. (3)), since both are acetone-soluble. Acetonitrile will dissolve $[Cp_2WH_2Ag(solvent)_n]_2^{2+}$, and above 0 °C it reacts immediately to give Ag^0, $Cp_2WH_3^+$ and $Cp_2WH(MeCN)^+$, making this compound a viable intermediate in eqn. (4). At the earliest observation times in CD_3CN, $[Cp_2WH_2Ag(solvent)_n]_2^{2+}$ shows ^1H NMR chemical shifts of 4.91 and -12.62 in a 5:1 intensity ratio; $Cp_2WH_3^+$ and $Cp_2WH(MeCN)^+$ are also evident. After 1 h (product peaks have now grown), the 4.91 chemical shift has moved to 4.86, while the hydride resonance is now at -12.53; these are in close agreement with the chemical shifts of $(Cp_2WH_2)_2Ag^+$. Reaction is complete at 3 h. The change of 'reagent' chemical shifts during the redox reaction (i.e. as reagent concentration diminishes) is characteristic of complex and rapidly-established equilibria (eqn. (5)). Attempts to record more structurally-useful ^1H NMR spectra by thawing frozen CD_3CN over solid $[Cp_2WH_2Ag(solvent)_n]_2(BF_4)_2$ in an NMR probe at -40 °C yielded no new information beyond that reported above.

$$\underset{\mathbf{6}}{(Cp_2WH_2Ag)_2^{2+}} \overset{MeCN}{\rightleftharpoons} (Cp_2WH_2)_2Ag^+ + Ag(MeCN)_n^+ \quad (5)$$

Mixed-oxidant systems

Given the fact that $(Cp_2WH_2)_2Cu^+$ is not oxidized by Cu^+, but that $(Cp_2WH_2)_2Ag^+$ is oxidized by Ag^+, two mixed-oxidant reactions were explored (eqns. (6) and (7)). Reaction of the W_2Ag adduct with Cu^+ as in eqn. (6) in CD_3CN (1:1 mole ratio) at 25 °C gives no reaction. The persistence of the silver hydride is confirmed by detection of Ag–H coupling in this reaction mixture at -70 °C. The 1:1 reaction of Ag^+ with $(Cp_2WH_2)_2Cu^+$ in MeCN at 25 °C, however, gives quantitative conversion to $Cp_2WH_3^+$ and $Cp_2WH(MeCN)^+$, as well as deposition of metal.

$$(Cp_2WH_2)_2Ag^+ + Cu(MeCN)_4^+ \longrightarrow \text{no reaction} \quad (6)$$

$$(Cp_2WH_2)_2Cu^+ + AgBF_4 \xrightarrow{MeCN} Cp_2WH_3^+ + Cp_2WH(MeCN)^+ + Ag + Cu \quad (7)$$

Discussion

Mechanism of Ag(I) oxidation of Cp_2WH_2

The silver(I) oxidation of Cp_2WH_2 in a one-to-one molar ratio results in quantitative production of equimolar **4** and **5** (eqn. (4)). A few observations must be accommodated by any oxidation mechanism. First, the ^1H NMR data suggest that $(Cp_2WH_2)_2Ag^+$ (**3**) participates in an equilibrium at room temperature (eqn. (3)), although the only species detectable by IR in solution is **3**. Compound **3** is stable in MeCN solution for at least 2 days. Second, if the oxidation of Cp_2WH_2 by Ag(I) is monitored periodically, a shift in the Cp and hydride resonances (0.05 ppm for Cp and 0.9 ppm for the hydrides) of the starting complex is observed as the reaction proceeds. Identical shifts are noted when $(Cp_2WH_2Ag)_2^{2+}$ (**6**) is dissolved in MeCN (i.e. the chemical shifts of the starting complex approach those of **3**). This observed shift is consistent with the presence of a preequilibrium involving **3** before the rate-determining electron-transfer. Finally, no other resonances are observed during the course of the oxidation other than those due to products and starting complex, even at 0 °C.

The three mechanisms in Scheme 1 all begin with cation **3**. Mechanism (I) makes no allowance for the presence of a pre-equilibrium and must consequently be discarded. Mechanism (II) offers two alternative (i.e. (IIa) or (IIb)) pre-equilibria involving **3** and implicates a one-to-one adduct $Cp_2WH_2AgS_n^+$ prior to electron transfer. In mechanism (III) is shown a pre-equilibrium step in which **3** binds Ag^+ to generate a two-to-two adduct, **6**, prior to redox. Several experimental facts support the choice of (III) over (II) as the appropriate mechanism. First, isolation of **6** due to its insolubility in THF supports its intermediacy. Second, the fact that $Cp_2WH_2AgS_n^+$ in mechanism (IIa) and (IIb) undergoes conversion to products is wholly inconsistent with the experimental fact that $(Cp_2WH_2)_2Ag^+$ (**3**), which in solution is in equilibrium with $Cp_2WH_2AgS_n^+$ (eqn. (3)), is stable for at least

$$\underset{\textstyle 3}{(Cp_2WH_2)_2Ag^+} + Ag^+ \xrightarrow{S} \text{products} \qquad \text{(I)}$$

$$\left.\begin{aligned} &3 \overset{S}{\rightleftharpoons} Cp_2WH_2AgS_n{}^+ + Cp_2WH_2 \\ &Cp_2WH_2 + Ag^+ \overset{S}{\rightleftharpoons} Cp_2WH_2AgS_n{}^+ \\ &Cp_2WH_2AgS_n{}^+ \xrightarrow{S} \text{products} \end{aligned}\right\} \text{(a)}$$

$$\text{(II)}$$

$$\left.\begin{aligned} &3 + Ag^+ \overset{S}{\rightleftharpoons} 2Cp_2WH_2AgS_n{}^+ \\ &Cp_2WH_2AgS_n{}^+ \xrightarrow{S} \text{products} \end{aligned}\right\} \text{(b)}$$

$$\begin{aligned} &3 + Ag^+ \overset{S}{\rightleftharpoons} \underset{\textstyle 6}{(Cp_2WH_2Ag)_2{}^{2+}} \\ &6 \xrightarrow{S} \text{products} \end{aligned} \qquad \text{(III)}$$

Scheme 1. (S = MeCN)

1 day in solution. Finally, compound **6** allows a very natural explanation for the production of equimolar **4** and **5** (see below).

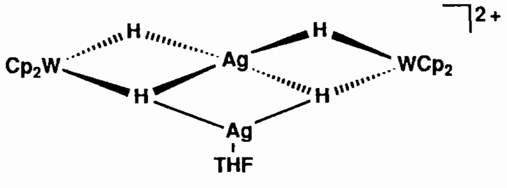
The intermediacy of complexes **3** and **6** leads to the unambiguous conclusion that Ag^+ oxidation of Cp_2WH_2 proceeds through an inner-sphere mechanism. This provides a very attractive explanation for the equimolar production of **4** and **5**. In contrast, Kochi and co-workers [14] found the *electrochemical* oxidation of Cp_2WH_2 produced the dimer $(Cp_2W)_2H_3{}^+$ (**7**). The mechanism they favored for the generation of **7** is presented in Scheme 2. In this mechanism, the key

$$\begin{aligned} &Cp_2WH_2 \xrightarrow{-e^-} Cp_2WH_2{}^+ \\ &Cp_2WH_2{}^+ \longrightarrow Cp_2WH^{\bullet} + H^+ \\ &Cp_2WH_2 + Cp_2WH^{\bullet} \longrightarrow Cp_4W_2H_3 \\ &Cp_4W_2H_3 \xrightarrow{-e^-} Cp_4W_2H_3{}^+ \end{aligned}$$

Scheme 2.

step is loss of H^+ from the radical cation $Cp_2WH_2{}^{+\bullet}$ to generate the free radical $Cp_2WH^{\bullet}$ which subsequently couples with the abundant Cp_2WH_2. The resulting $(Cp_2W)_2H_3{}^{\bullet}$ is then further oxidized to form the observed product **7**. In the contrasting *chemical* oxidation of Cp_2WH_2, the Ag^+ acts to hold to Cp_2WH_2 substrates together in **6**. The geminate character of **6** holds all reactants together in the same solvent cage where facile processes such as $H^{\bullet}$ or H^+ transfer can occur after the rate-determining intramolecular electron transfer. Thus, the radical cation $Cp_2WH_2{}^+$ of the electrochemical route (Scheme 2) is irrelevant in the Ag^+ oxidation. As further proof, we find that the authentic outer-sphere oxidant, Cp_2Fe^+, which lacks the ability to form intermediates such as **6**, does not yield **4** and **5** in equimolar amounts but rather in a 5:2 ratio, respectively*.

Speculation about the structure of **6** is based on an analogous compound (**B**) synthesized by the Bulychev group [6]. This structure, as well as our observation that THF is present in the ^1H NMR spectrum of **6** in CD_3CN even after extended exposure to vacuum, suggests structure **C** for **6**. Integration of these THF resonances against the Cp signal suggests one THF per mole of **6**.



C

Structure, bonding and spectral properties of 1

An integrated description of the structure, spectral properties and bonding of **1** merits further discussion. A central question is whether the Mo/Cu linkage involves hydride bridging or only Mo → Cu dative bonding. The Cu–H bond distance of 1.68 Å in **1** shows a significant Cu–hydride interaction**. When **1** is compared to free Cp_2MoH_2, the dramatic shift to lower frequencies of the hydride stretch in the IR in going from Cp_2MoH_2 to **1** is consistent with formation of a μ-H. Moreover, if the Mo–H moiety were experiencing no bonding to Cu, it would be expected that the H–Mo–H angle would increase greatly in going from Cp_2MoH_2 to **1** as the result of $(Cp_2H_2Mo)_2 \rightarrow Cu$ donation. The observed H–Mo–H angle of 76.5° of **1** is basically unchanged from that of Cp_2MoH_2 itself. This compares to the compound Cp_2TaH_3 containing an outer H–Ta–H angle of 125.8(5)° [17].

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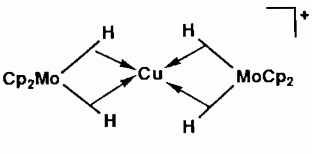
*Cp_2Fe^+ oxidations of monohydrides have been shown to be followed by rapid proton transfer to unoxidized hydride, thus accounting here for the enhanced yield of $Cp_2WH_3{}^+$. The product distribution in such oxidations has been shown to be concentration dependent [15].

**For $[CH_3C(CH_2PPh_2)_3Cu]_2(\mu\text{-}H)_2$, the Cu–H distances were found to average 1.73(11) Å [16].

A qualitative molecular orbital analysis of the bonding between the two Cp_2MoH_2 units and Cu(I) in compound **1** is facilitated by two factors: both the structure of **1** and the frontier orbitals of Cp_2MoH_2 and Cu(I) are well known [18]. A simple MO scheme, based purely on symmetry arguments, can be constructed for the idealized tetrahedral conformer of **1** (see Fig. 3). In this D_{2d} conformer, the frontier orbitals of two Cp_2MoH_2 units are of a_1, b_2 and e symmetry types and contain a total of 12 electrons. The frontier orbitals of Cu(I) are taken to be the empty 4s and 4p orbitals since the filled d-block is too low in energy to overlap significantly. Therefore, the Cp_2MoH_2 molecules are acting as Lewis bases by donating electrons into the empty orbitals of the Lewis acid, Cu(I).

When these units combine, four bonding orbitals of a_1, b_2, and e symmetry are formed along with two non-bonding interactions. Upon filling these molecular orbitals with the available 12 electrons of the two Cp_2MoH_2 units, it is apparent that the Cp_2MoH_2 are donating a total of eight electrons to Cu(I) and that the high-lying a_1 and b_2 non-bonding orbitals are derived primarily from the lone pairs present on Cp_2MoH_2. This MO picture suggests a valence bond description **I** in which each pair of Mo–H bonding electrons is donated to the 'naked' Cu(I), for a total of eight electrons donated, and where a pair of electrons resides on each Mo. In description **I**, the Cu(I) center attains the 18-electron configuration. Such three-center two-electron bonding interaction has been suggested by Green and co-workers to explain bonding in several species containing bridging hydrides [19]. It is evident from the MO diagram that although the lone-pair orbitals on each Cp_2MoH_2 unit are of the correct symmetry for overlap with an s and p orbital of Cu(I), the overlap would not be significant because of the unsuitable directional characteristics of



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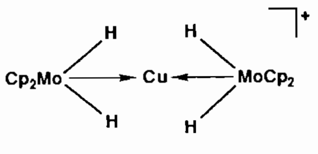

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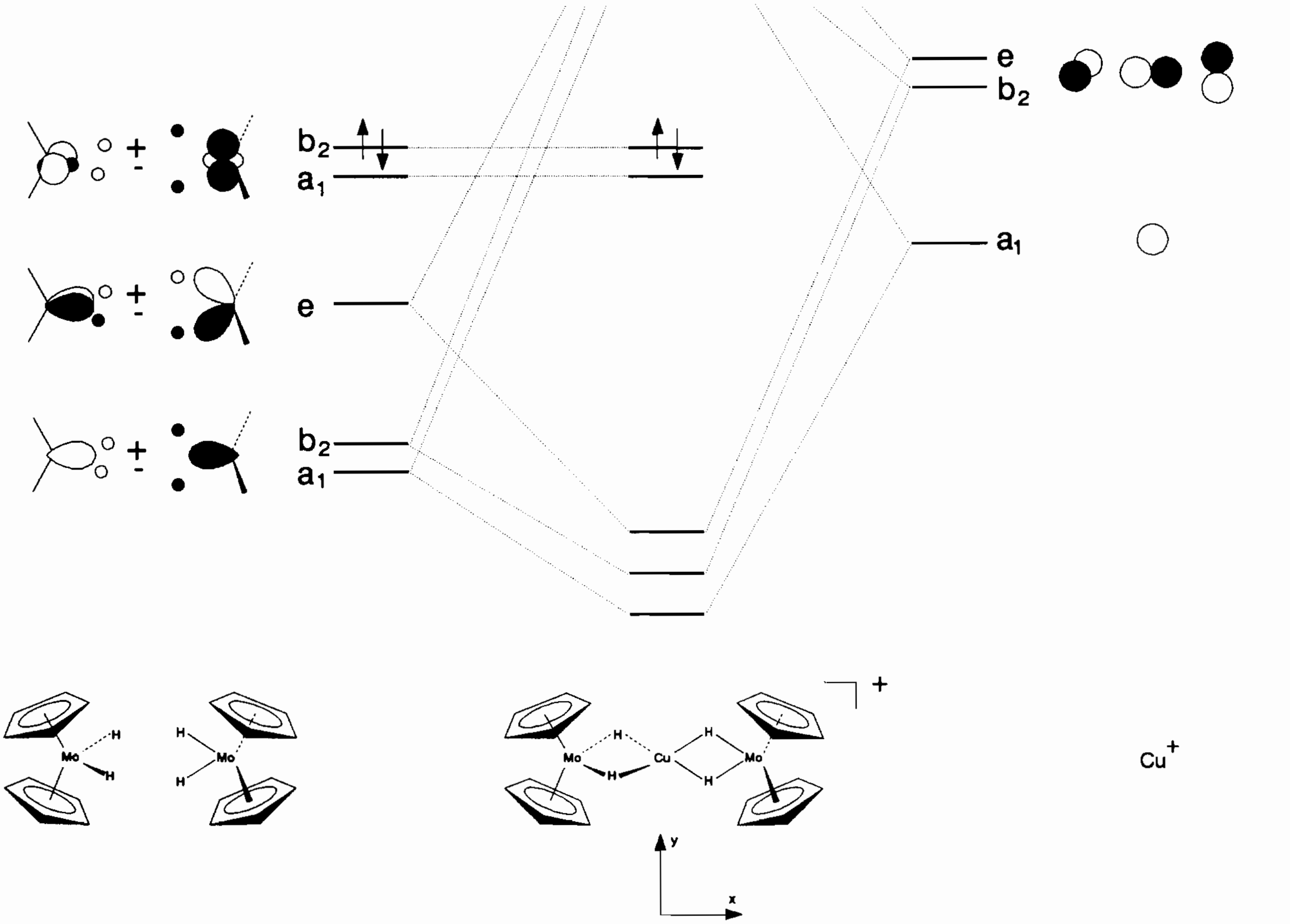

Fig. 3. Molecular orbital diagram for $(Cp_2MoH_2)_2Cu^+$ with quasi-tetrahedral symmetry at copper (D_{2d} symmetry).

the orbitals involved. Thus, a bonding picture involving direct donation of these lone-pair orbitals to Cu (see II) is probably *not* the best description.

The other limiting geometrical conformer possible for **1** is square planar at Cu (D_{2h}). The degenerate e set (of D_{2d}) is split into a b_{2g} and b_{3u} orbital. In this conformer only three bonding interactions are permitted by symmetry. The b_{2g} orbital is non-bonding. This loss of bonding to copper mimics the situation for planar versus tetrahedral carbon, since copper is modelled here as having only s and p orbitals. Thus, the square-planar conformer is predicted to be the less stable of the two. This prediction is confirmed by experiment since, although two independent cations are present in the unit cell of **1**, neither is rigorously square planar. The actual structure found is between the two limiting cases of D_{2d} and D_{2h}, and we attribute the absence of uniformly D_{2d} symmetry in the solid state to packing forces being comparable in energy to (and opposing) the energetic preference for D_{2d} over D_{2h}.

The non-hydride species $Cp_2M(SR)_2$ (M = Ti, Nb, Mo and W) function as rather conventional bidentate ligands towards $M(CO)_4$ (M = Cr, Mo, W) [20, 21], $FeCl_2$ [22], $Rh(\eta^3\text{-allyl})_2^+$ [23] and Ni^{2+} [24]. The compounds isolated here show that replacement of the –SR ligands by hydrides leads to no apparent reduction in the donor ability of the metallocene complexes in spite of the reduction in valence electron count. The earliest examples of 1:1 adducts of dihydrides include $Cp_2MH_2ER_3$ (M = Mo and W; E = B and Al) [25] and $Cp_2MH_2[M'(CO)_5]$ (M = Mo and W; M' = Cr, Mo and W) [26] although hydride bridging was originally thought to be absent in all of these. The $ZnBr_2$(dimethylformamide) adduct of Cp_2MoH_2 was proposed to have bridging hydrides [27] and these were established crystallographically in the $Rh(PPh_3)_2^+$ adduct [28]. The Bulychev group has established the presence of two hydride bridges in both $Cp_2MoH_2FeCl_2(THF)$ [29] and $(Cp_2MoH_2FeBr_2)_2$ [30]. A related μ-monohydride case includes the $Fe(CO)_4$ adduct of $Cp_2NbH(CO)$ [31]. An interesting case where Cp_2WH_2 can donate either one or two of its available hydrides to a Pt center has been reported by Venanzi and co-workers [32].

In all of the cited literature containing a μ-H interaction, the reported IR absorptions consist of broad bands of lowered frequency (compared to the terminal hydride precursor) or even of unobserved bands. The IR absorption assigned to μ-H motions in compounds **1, 2, 3** and **7** are marked by exceptional breadth (50–100 cm^{-1} half width); they are much broader than the terminal hydride absorptions in the precursors Cp_2WH_2 and Cp_2MoH_2, which are themselves somewhat broad (~ 30 cm^{-1} half width). Kaesz and Saillant have noted this effect for μ-hydrides in three- and four-metal clusters [33]. Although the extreme manifestation of this effect may be the erroneous conclusion that μ-H units are absent, we propose that this breadth be taken as supporting evidence for a bridging role of hydride ligands; 'low' frequencies, however, remain the primary criterion.

The question of the origin of this broadening may be pursued by recognizing that the M...H...M' bears a kinematic similarity to the O...H...O unit and that such traditional hydrogen bonding exhibits characteristically broad IR spectra in the OH stretching region. The origin of broad IR absorptions in all hydrogen-bonded linkages has attracted much attention, but definite explanation remains elusive, or at least controversial, and without resolution [34]. Fermi resonance has been argued [35]. Another model [36] is based upon strong coupling between several vibrational motions of the triatom unit; in essence, a breakdown of the independent vibrational mode assumption is invoked, and the physical picture of the vibrational motions is consequently obscure. Another model [37] attributes broadening to ready perturbations of weak bonds by environmental effects; a 'disordered' medium leaves different A...H...B oscillators in distinct potential wells with the consequence of a myriad of quite similar vibrational frequencies. This last explanation is at least plausible for the compounds studied here, since M–H bonds are among the 'softest' (i.e. most readily deformed) of bonds. For example, the terminal Mo–H bond in Cp_2MoH_2 can be calculated to have a stretching force constant of 2.1×10^5 dyne/cm, compared [38] to the weakest hydrogen halide (HI, at 3.1×10^5), OH in H_2O (7.76×10^5) and even Si–H at 2.8×10^5 dyne/cm. A bridging transition metal hydride is thus particularly plastic in response to solvent, solid lattice, or counterion influences. Finally, the structure of $(Cp_2MoH_2)_2Cu^+$, showing two conformers, brings reality to the conjecture that the medium can generate several related but distinct oscillators.

Finally, one must address the question of why Ag(I) effects the oxidation of Cp_2WH_2 whereas Cu(I) does not. The answer to this question is facilitated by the electrochemical data for these reagents. Kochi and co-workers [14] have found the oxidation potential of Cp_2WH_2 in MeCN to be −0.350 V versus SCE [39]. The reduction potentials of Ag(I) [40] and Cu(I) [41] are found to be +0.37 and −0.36 V versus SCE in MeCN, respectively. Obviously, Cu(I) is a much weaker oxidant than Ag(I) in MeCN*. Indeed, the potential for Cu(I) oxidation of Cp_2WH_2 is negative and thus is unfavorable. Still, it is interesting to note that oxidation of **2** occurs when Ag(I) is added and no reaction (or

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*Direct oxidation of Cu^0 by Ag^+ in MeCN has been demonstrated [42].

evidence of complex formation analogous to **6**) occurs when Cu(I) is added to **2**. Thus, the primary oxidation must be initiated by the stronger Ag(I) oxidant, thereby creating a cluster radical cation that is easily oxidized by the weaker Cu(I) oxidant. This is confirmed by the opposite crossover experiment in which Cu(I) does not initiate oxidation of $(Cp_2WH_2)_2Ag^+$. These experiments also prove that no exchange of electrophile is occurring on the order of hours in these systems, although this type of exchange has been observed by Stone and coworkers in cluster chemistry involving Ag^+, Au^+ and Cu^+ phosphines [43]. Obviously, Cp_2WH_2 shows a marked preference to bind to Ag(I). This is probably because of the greater electrophilicity of Ag(I) over Cu(I) which is consistent with the notable oxidation potential difference between the two monocations. An additional feature of the structure (**C**) proposed for **6** is the inequivalence of the two oxidant sites. This structural inequivalence allows retention of distinct oxidizing power of the two electrophilic monocations in the two different $(Cp_2MH_2)_2(Ag)(Cu)^{2+}$ species, consistent with the results in eqns. (6) and (7).

Conclusions

In this study, the results of the interaction of Cu(I) with Cp_2MH_2 (M = Mo and W) and Ag(I) with Cp_2WH_2 are presented. In the case of Cu(I) and M = Mo, the crystal structure of the 2:1 adduct, $(Cp_2MoH_2)_2Cu^+$ (**2**) is reported. For **2**, an MO scheme shows the predominance of $Mo\text{–}H \rightarrow Cu^+$ donation over $H_2Mo \rightarrow Cu^+$ donation. Proton NMR evidence is presented for the intermediacy of $(Cp_2WH_2)_2Ag^+$ (**3**) and $(Cp_2WH_2Ag)_2^{2+}$ (**6**) in the Ag(I) oxidation of Cp_2WH_2 to $Cp_2WH_3^+$ and $Cp_2WH(MeCN)^+$. A proposed reaction scheme suggests the importance of the geminate (cluster) character of intermediates **3** and **6** in the production of the oxidation products. This feature is sufficient to explain the different products obtained in the chemical versus electrochemical oxidation of Cp_2WH_2.

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