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The X-ray structure of the hydroxycarbene complex $[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+[CF_3SO_3]^-$ { *facial*-[1,3-bis(diphenylphosphino)propane(methylhydroxycarbene)tricarbonylmanganese(I)]} triflate

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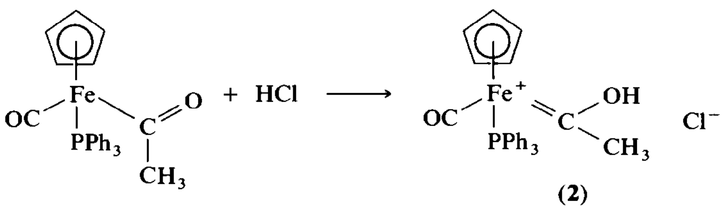
Abstract

The cationic octahedral manganese(I) hydroxycarbene complex $[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+$ has been synthesized and isolated as its triflate salt, and its structure fully determined by X-ray diffraction. A comparison of our cationic Mn^I methylhydroxycarbene complex to the neutral isoelectronic Cr^0 and Mo^0 phenylhydroxycarbene structures reported in the literature reveals a number of surprising differences and similarities. In the Cr and Mo complexes the metal fragment and the hydroxy hydrogen are positioned *syn*(*Z*-isomer) giving the conformational isomer often seen in alkoxycarbenes. In contrast, in our Mn complex, these substituents are found in the alternate *anti* conformation (*E*-isomer). In addition, dimers are observed in the solid state due to a much more intricate network of hydrogen bonds. Nevertheless, in each of these octahedral isoelectronic hydroxycarbene complexes, the orientation of the metal framework and the carbene moiety with respect to each other is remarkably similar. A twist of approximately 34° about the M–C(carbene) bond and away from the fully eclipsed electronically favored geometry is observed in all three complexes.

Introduction

Hydroxycarbenes complexes have long been of general interest to practitioners of organometal chemistry, but of particular interest to those concerned with intermediates in the transition metal catalyzed reduction of carbon monoxide (the Fischer–Tropsch reaction). Probably the first example of a well-characterized species of this nature, **2**, was obtained [1] by protonation of the acetyliron complex **1**:



(**1**)

(**2**)

0022-328X/91/$03.50

Since then many other transition metal hydroxycarbene complexes of transition metals have been reported, some cationic, and some neutral [2].

Our interest in hydroxycarbene complexes developed from our study [3] of the behavior, on treatment with strong protic acids, of the acylmanganese carbonyl complexes, $L_2(CO)_3Mn-C(O)R$, **3**. These acyl complexes undergo slow spontaneous thermal decarbonylation in solution. In the presence of trifluoromethylsulfonic acid (triflic acid) the rate of decarbonylation is retarded owing to the reversible formation of corresponding hydroxycarbene complexes but eventually quantitative conversion to the alkylmanganese carbonyl complex occurs. The hydroxycarbenes can be isolated by precipitating them before they have the opportunity to decarbonylate.

Results and discussion

The synthesis and infrared spectra of the hydroxycarbenes

Treatment of $CH_3Mn(CO)_5$ with 1,3-bis(diphenylphosphino)propane (DPPP) gives the *fac*-tricarbonyl-manganese acyl complex, $(DPPP)(CO)_3Mn-C(O)CH_3$, **4**, and protonation of it with triflic acid gives the ionic hydroxycarbene complex, $[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+[SO_3CF_3]^-$, **5**. The infrared spectrum of this complex in the terminal carbonyl region shows a strong higher-frequency shift in all three bands as compared to its precursor **4**, (Table 1). This is the expected effect [4] of the increased positive charge on the manganese which reduces *d*-electron back-bonding into the terminal CO's with the resulting greater triple bond character in the coordinated CO. The acyl carbonyl band observed in the spectrum of **4** at 1570 cm^{-1} is, as expected, absent in the protonated species. The bottom portion of Table 1 lists some C–F and SO_3 stretching bands in ionic triflate salts [5,6]. Although unambigous assignments are not possible due to mixing of CF_3 and SO_3 vibrational modes [6–8] there is nevertheless an interesting correspondence in these bands between the covalent complex, $Mn(CO)_5(CF_3SO_3)$ and those of our complex, **5**. It

Table 1

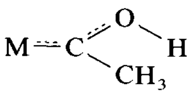
Infrared stretching frequencies (cm^{-1}) for manganese carbonyls and triflates

Compound [a]	ν(C=O) (terminal)		Ref.
fac-$(DPPP)(CO)_3Mn\text{-}C(O)CH_3$	2001 (s), 1924 (s), 1911 (s)		this work [b]
fac-$[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+$ $CF_3SO_3^-$	2026 (s), 1967 (s), 1955 (s)		this work [c]
mer, trans-$[(PPh_3)_2(CO)_3Mn{=}C(OH)H]^+$ *p*-$CH_3C_6H_4SO_3^-$	2045 (w), 1960 (s, br)		4 [c]
mer,trans-$[(PPh_3)_2(CO)_3Mn{=}C(OH)H]^+$ BF_4^-	2045 (w), 1950 (s, br)		4 [c]
	ν(C–F)	ν(S=O)	
fac-$[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+$ $CF_3SO_3^-$	1232 (s), 1206 (s)	1176 (m), 1015 (m)	this work [c]
$Mn(CO)_5(CF_3SO_3)$	1234 (m), 1202 (s)	1179 (m), 1013 (m)	5 [c]
Na^+ $CF_3SO_3^-$	1280 (vs, br), 1232 (m)	1268 (s), 1036 (s)	6 [d]
Ag^+ $CF_3SO_3^-$	1270 (vs, br) 1237 (s)	1167 (s), 1043 (vs)	7 [e]
PPN^+ $CF_3SO_3^-$		1182 (m), 1028 (s)	5 [d]

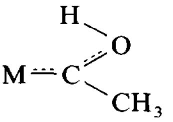
[a] DPPP is $Ph_2PCH_2CH_2CH_2PPh_2$. The bottom four compounds were examined as mulls; all others were examined as solutions in methylene chloride. Infrared spectra were taken in [b] chloroform, [c] methylene chloride, [d] Nujol mulls, or [e] pressed CsI pellets.

should be noted that the crystal structure of **5** shows that the triflate anion is bonded to the cation through water molecules and the observed spectral similarities may possibly result from these hydrogen bonding interactions. We were unable to ascertain with certainty any band above 2200 cm^{-1} that could be unambiguously assigned to the ν(O–H) stretch of the hydroxy carbene.

The C(carbene)–O bond stretch is of considerable diagnostic value. This single bond has appreciable double bond character and hence there is a barrier to rotation around it giving rise to stable *E* and *Z* isomers (or, as frequently referred to in the literature [9] *anti* and *syn* with respect to the H atom and the metal fragment; we prefer the unambiguous *E* and *Z* nomenclature):



(*E*-isomer (*anti*))



(*Z*-isomer (*syn*))

It has been suggested [9] that bands in the 1250–1300 cm^{-1} region are characteristic of the C(carbene)–O stretch of the *E*-form of the hydroxy-carbene in solution but we observed no bands in this region. On the other hand absorption at 1234 cm^{-1} is assumed to characterize the *Z*-form. In fact our X-ray analysis shows our compound to have this conformation (*vide infra*); however we were unable to confirm that the spectrum of our compound shows a C–O stretch at this frequency because of the presence of a triflate band in the same region. Unfortunately the BF_4^- salts of hydroxycarbene complexes are unstable.

The crystal structure of fac-$[(DPPP)(CO)_3Mn{=}C(OH)CH_3]SO_3CF_3 \cdot H_2O$, *5*

Atomic coordinates and selected bond distances and angles for the methylhydroxycarbene complex salt, **5**, are summarized in Tables 2 and 3, respectively. Its solid state structure consists of discrete molecular cations and anions and a water of hydration. The compound exists as dimers in the crystal through a network of hydrogen bonds. A view of the *facial* octahedral cation is shown in Fig. 1, and the hydrogen-bonding in the solid state is depicted in Fig. 2.

The octahedral cation contains a six-membered (DPPP)Mn metallacyclic chelate ring with a CO ligand bound *trans* to each of the coordinated phosphorus atoms. The Mn–P and Mn–CO distances [2.356(1), 2.357(1), 1.796(5), 1.805(6) Å] in this equatorial plane are in reasonably good agreement with the attributes of the *trans* OC–Mn–P moiety in the methoxycarbonyl complex $(PPh_3)(CO)_4Mn{-}C(O)OCH_3$ [2.350(4), 1.81(2) Å] [10]. The axial sites of the octahedral Mn complex are occupied by a methylhydroxycarbene ligand and a third CO molecule, respectively. The observed Mn–C(carbene) and *trans* Mn–CO distances are 1.968(4) and 1.852 (4) Å, respectively, and are comparable to values reported for *trans* OC–Mn–C(carbene) moieties in related methoxycarbene complexes, e.g., $(PPh_3)_2(CO)_3Mn{=}C(H)OCH_3$ [1.947(4), 1.849(4) Å] [4] and $[(CO)_5Mn](CO)_4Mn{=}C(Ph)OCH_3$ [1.950(5), 1.840(5) Å] [11]. The 1.968(4) Å Mn–C(carbene) bond in our methylhydroxycarbene complex is slightly longer than those found in these other octahedral Mn carbene compounds, but is significantly shorter than the single bond distances

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$·H$_2$O, **5** [a]

Atom	*x*	*y*	*z*	U_{eq} [b]
Mn	1430(1)	4154(1)	2669(1)	48(1)
P(1)	2853(1)	4513(1)	1403(1)	51(1)
P(2)	2511(1)	3313(1)	3612(1)	45(1)
O(1)	−4(3)	1684(3)	1728(3)	85(1)
O(2)	−406(3)	3839(3)	4210(3)	84(2)
O(3)	−1(4)	5191(5)	1548(3)	113(2)
O(4)	3511(3)	6045(3)	3591(2)	65(1)
C(1)	563(4)	2624(4)	2087(3)	60(2)
C(2)	328(4)	3945(4)	3620(3)	60(2)
C(3)	571(5)	4787(5)	1968(4)	73(2)
C(4)	2393(4)	5755(3)	3312(3)	56(2)
C(5)	1904(6)	6730(4)	3554(5)	88(3)
C(6)	4407(4)	4671(4)	1754(3)	59(2)
C(7)	4478(3)	3628(4)	2280(3)	62(2)
C(8)	4145(3)	3686(3)	3360(3)	54(1)
C(9)	3131(4)	5908(4)	829(3)	64(2)
C(10)	2709(7)	5898(5)	−111(4)	103(3)
C(11)	2894(9)	6963(6)	−514(6)	143(5)
C(12)	3499(8)	8034(6)	6(6)	126(4)
C(13)	3928(7)	8069(5)	911(5)	103(3)
C(14)	3757(5)	7012(4)	1326(4)	81(2)
C(15)	2406(4)	3358(4)	364(3)	63(2)
C(16)	1245(5)	3001(5)	−33(3)	74(2)
C(17)	849(6)	2095(5)	−798(4)	89(3)
C(18)	1609(8)	1537(6)	−1160(5)	107(3)
C(19)	2776(7)	1886(6)	−787(4)	97(3)
C(20)	3170(5)	2789(5)	−25(4)	76(2)
C(21)	2554(3)	3608(3)	4952(3)	50(1)
C(22)	2240(4)	4513(4)	5441(3)	60(2)
C(23)	2274(5)	4685(4)	6463(4)	74(2)
C(24)	2596(5)	3926(5)	6993(4)	73(2)
C(25)	2921(5)	3038(4)	6526(4)	75(2)
C(26)	2901(4)	2852(4)	5515(3)	63(2)
C(27)	1831(3)	1670(3)	3477(3)	52(1)
C(28)	664(4)	1116(3)	3838(3)	60(2)
C(29)	92(5)	−120(4)	3731(4)	69(2)
C(30)	652(5)	−818(4)	3279(4)	83(2)
C(31)	1809(6)	−298(4)	2930(5)	93(3)
C(32)	2404(4)	951(4)	3029(4)	72(2)
S	4363(2)	9142(2)	6938(2)	105(1)
O(5)	4627(6)	8983(5)	7863(4)	159(4)
O(6)	4176(8)	8025(6)	6311(5)	205(5)
O(7)	5093(6)	10165(6)	6596(7)	217(5)
C(33)	2922(9)	9162(10)	6797(14)	203(7)
F(1)	2560(8)	9096(9)	5884(7)	258(7)
F(2)	2124(6)	8220(10)	7189(7)	309(6)
F(3)	2831(9)	10018(10)	7325(12)	449(10)
O(8)	4763(4)	8041(3)	4416(3)	98(2)
H(4)	3994(45)	6908(45)	3857(36)	80

[a] DPPP is $Ph_2PCH_2CH_2CH_2PPh_2$. [b] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond distances (Å) and angles (°) for *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$·H$_2$O, 5 [a]

Mn–P(1)	2.356(1)	C(1)–O(1)	1.147(5)
Mn–P(2)	2.357(1)	C(2)–O(2)	1.158(6)
Mn–C(1)	1.852(4)	C(3)–O(3)	1.151(9)
Mn–C(2)	1.796(5)	C(4)–O(4)	1.285(6)
Mn–C(3)	1.805(6)	C(4)–C(5)	1.497(8)
Mn–C(4)	1.968(4)	O(4)–H(4)	1.02(4)
P(1)–Mn–P(2)	93.5(1)	C(1)–Mn–C(4)	177.8(2)
P(1)–Mn–C(1)	90.9(1)	C(2)–Mn–C(3)	89.6(2)
P(1)–Mn–C(2)	177.1(2)	C(2)–Mn–C(4)	89.7(2)
P(1)–Mn–C(3)	87.9(2)	C(3)–Mn–C(4)	90.7(2)
P(1)–Mn–C(4)	88.8(1)	Mn–C(1)–O(1)	178.0(5)
P(2)–Mn–C(1)	88.3(2)	Mn–C(2)–O(2)	177.0(5)
P(2)–Mn–C(2)	89.0(2)	Mn–C(3)–O(3)	177.7(5)
P(2)–Mn–C(3)	178.6(2)	Mn–C(4)–O(4)	122.1(4)
P(2)–Mn–C(4)	89.5(2)	Mn–C(4)–C(5)	124.3(4)
C(1)–Mn–C(2)	90.6(2)	C(5)–C(4)–O(4)	113.6(4)
C(1)–Mn–C(3)	91.5(2)	C(4)–O(4)–H(4)	119(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits; DPPP is Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$.

found in Mn acyls, e.g., [(PhO)$_3$P)]$_3$(CO)$_2$Mn–C(O)CH$_3$ [2.062(7) Å] [12], and (CO)$_4$Mn[C(O)CH$_3$][C(O)Ph] [2.05(1), 2.09(1) Å] [13].

Data describing the geometry and orientation of the methylhydroxycarbene

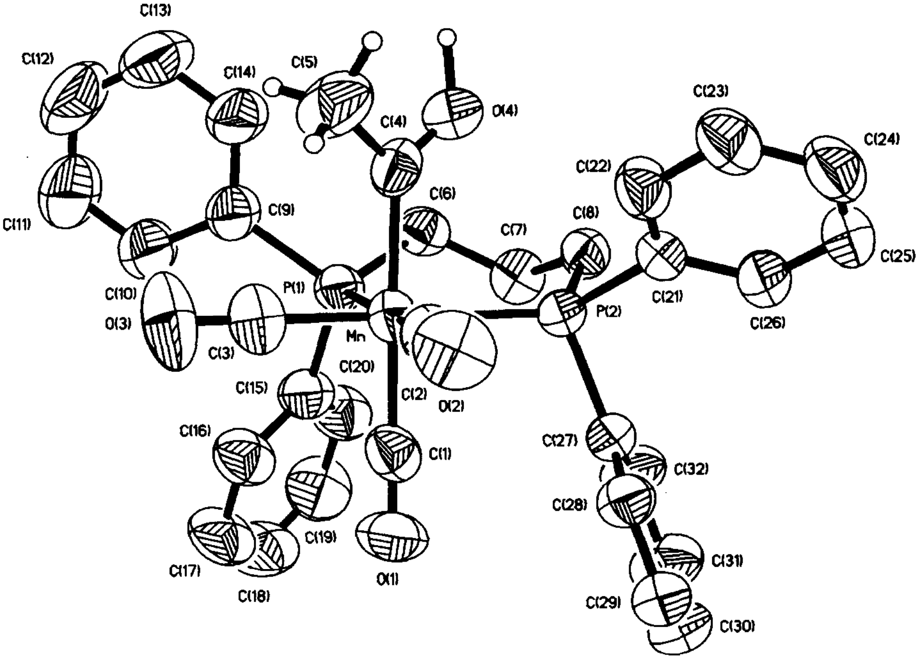


Fig. 1. Molecular structure of the *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]$^+$ cation. Ellipsoids are drawn at the 50% probability level.

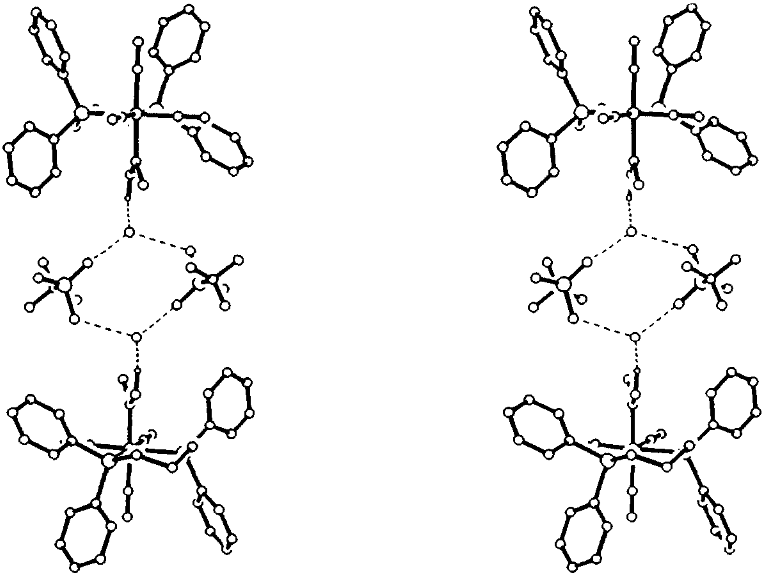


Fig. 2. A stereo view of the hydrogen-bonding interactions between pairs of *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$·H$_2$O formula units in the solid state (DPPP is Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$).

ligand in our structure, as well as selected structural information on previously reported hydroxycarbene complexes by others [14,15] are summarized in Table 4. In spite of their differing transition metal centers and ligands, the observed M–C(carbene)–O and M–C(carbene)–R angles in these hydroxycarbene complexes are in remarkably good agreement. The Mn–C(carbene)–O angle [122.1(4)°] is slightly more acute than the Mn–C(carbene)–R angle [124.3(3)°] as is generally observed in related Mn alkoxycarbene compounds, e.g., [(CO)$_5$Mn](CO)$_4$Mn=C(Ph)OCH$_3$ [119.4(3), 125.0(3)°] [11], [(1-naphthyl)(CH$_3$)(Ph)Ge](CO)$_4$Mn=C(CH$_3$)OEt [119(1), 127(2)°] [16] and (Ph$_3$P)$_2$(CO)$_3$Mn=C(H)OCH$_3$ [123.9(4)°, –] [4]. On the other hand, the R–C(carbene)–O angle in our Mn complex is significantly more obtuse than the values observed in the Cr and Mo derivatives [113.6(4) versus 107(1) and

Table 4

Geometry and orientation of hydroxycarbene ligands (°) [a]

	Mn [b]	Cr [c]	Mo [d]
M–C(carbene)–O	122.1(4)	122(1)	124.0(4)
M–C(carbene)–R	124.3(3)	130(1)	128.1(5)
R–C(carbene)–O	113.6(4)	107(1)	107.8(5)
L–M–C(carbene)–O [e]	32.8	36.6	37.4
dihedral angle [f]	33.4	34.3	33.9

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] *fac*-[(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)(CO)$_3$Mn=C(OH)CH$_3$]$^+$, this work. [c] (CO)$_5$Cr=C(OH)Ph, ref. 14. [d] (Ph$_2$POCH$_2$CH$_2$OCH$_2$-)$_2$(CO)$_3$Mo=C(OH)Ph, ref. 15. [e] L is the *cis* ligating atom on the metal which is nearest to the hydroxy oxygen atom. [f] Based on the two planes defined by the following sets of atoms: Plane 1—L, M, C(carbene), and the two ligating atoms *trans* to L and C(carbene). Plane 2—M, C(carbene), and R, where R is the carbon of the methyl or phenyl substituent attached to C(carbene).

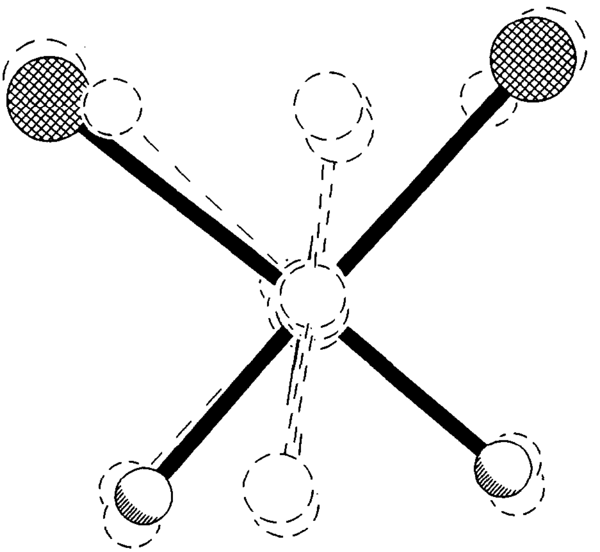


Fig. 3. A perspective view of the similarity in orientation of the hydroxycarbene moieties in *fac*-$[(DPPP)(CO)_3Mn{=}C(OH)CH_3]^+$, *fac*-$(Ph_2POCH_2CH_2OCH_2)_2(CO)_3Mo{=}C(OH)Ph$, and $(CO)_5Cr{=}C(OH)Ph$ (DPPP is $Ph_2PCH_2CH_2CH_2PPh_2$).

107.8(5)°] [14,15]. The large angular difference noted above is consistent with the observed *anti* conformation (*E*-isomer) of the hydroxy hydrogen atom and the metal fragment about the carbene C–O bond in our Mn compound versus the alternate *syn* conformation (*Z*-isomer) observed and proposed for the Cr and Mo derivatives, respectively. Interestingly, in spite of this difference in corformation, metal centers and ligands, the orientation of the hydroxycarbene moieties within these three compounds are surprisingly similar (Fig. 3). All three complexes show a twist [about the M–C(carbene) bond] of roughly 34° away from the electronically preferred totally eclipsed conformation. Because of the smallness of the barrier to rotation about the M–C(carbene) bonds in transition metal carbenes, [17,18] the similarity of the observed twists in these hydroxycarbenes would seem to imply that packing and hydrogen-bonding forces are likely to be only minor contributors to the conformations found in the solid state. The major contributor seems to be the local steric forces near the carbene carbon which would appear to be comparable in all three of these compounds in spite of their different constitutions. The attributes of the Mn=C–O–H fragment are comparable in values to O=C–O–H carboxylic acid groups. The observed C–O bond is 1.285(6) versus 1.31(2) Å in organic acids, while the O–H bond is 1.02(4) versus 1.02(2) Å [19]. The slight shortening in the C–O bond and the near planarity of the $Mn{=}C(OH)CH_3$ unit as well as the lengthening of the Mn–C(carbene) bond mentioned above are all consistent with a partial degree of π-donation of electron density from the hydroxy oxygen atom to the carbene carbon atom. The C(carbene)–C bond of 1.497(8) Å in the $Mn{=}C(OH)CH_3$ unit is slightly shorter than those in related Mn complexes, but in good agreement with the value of 1.50(1) Å observed in O=C(OH)R carboxylic acids [19].

As shown in Fig. 2, dimers consisting of two formula units of $[(DPPP)(CO)_3Mn{=}C(OH)CH_3]SO_3CF_3 \cdot H_2O$ are observed in the solid state structure of this methylhydroxycarbene complex. Each water molecule in the structure is hydrogen-

Table 5

Hydrogen-bonding interactions for *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$·H$_2$O, 5 [a]

O(4)···O(8)	2.479(4)	O(4)···O(8)···O(6)	107.2(2)
O(6)···O(8)	2.682(9)	O(4)···O(8)···O(7′)	113.5(2)
O(7′)···O(8)	2.625(10)	O(6)···O(8)···O(7′)	121.9(3)
O(4)–H(4)	1.02(4)	O(4)–H(4)···O(8)	168(6)
H(4)···O(8)	1.48(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits; Symmetry code: ′ = (1 − x, 2 − y, 1 − z); DPPP is Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$.

bonded to the OH functionality of the Mn hydroxycarbene cation and an oxygen atom from each of the two symmetry related triflate anions. The relevant structural information is summarized in Table 5. Hence, all three hydroxycarbene transition metal complexes that have been crystallographically examined to date have been found to contain hydrogen-bonding interactions, but each of a different nature. A single intermolecular hydrogen-bond to an acetonitrile of crystallization was observed with the Cr derivative [14], while a single intramolecular hydrogen-bond to the diphosphinite backbone in the Mo derivative was suggested [15]. In the Mn structure reported here, the hydroxycarbene also forms a single intermolecular hydrogen-bond (in this case, to a water of crystallization), however, additional interactions between the waters and the triflate anions in the lattice are observed giving a solid state structure consisting of aggregated dimers (Fig. 2).

Experimental

Materials and physical measurements

DPPP was obtained from Strem Chemicals and triflic acid was purchased from Aldrich. Both were used as received. Tetrahydrofuran (THF) was freshly distilled under N$_2$ from benzophenone ketyl. All other solvents and chemicals were reagent grade and were used without further purification. Reactions were carried out in oven-dried glassware under an inert atmosphere. Infrared spectra were recorded on a Perkin–Elmer Model 1600 FT-IR spectrophotometer, and low resolution mass spectroscopic measurements were obtained on an HP 5995 GC/MS instrument. Melting points were determined using open-end capillaries with a Mel–Temp apparatus and are uncorrected.

Preparation of (DPPP)(CO)$_3$MnC(O)CH$_3$, 4

This acetylmanganese starting material was prepared from (CO)$_5$MnCH$_3$ and DPPP using the literature method as a basis [20]. A solution of 0.878 g (4.18 mmol) of (CO)$_5$MnCH$_3$ [3] and 1.72 g (4.17 mmol) DPPP in about 50 mL tetrahydrofuran (THF) was stirred at room temperature under argon for about 22 h. The volume was then reduced to about 5 mL on a roto-evaporator and 50 mL pentane added and the solution placed in the freezer. The pale yellow crystals which precipitated were separated by filtration and air dried giving about 1.21 g (~ 50%). The IR spectrum in CHCl$_3$ showed the expected bands for terminal carbonyl bands at 2001(s), 1924(s,br) and 1911(s), and the acyl carbonyl band at 1570(s) cm^{-1} in accordance with the literature [20]. The low resolution mass spectrum did not show the parent ion but did give a large peak at 510.44 corresponding to the loss of 3CO from the parent ion.

Table 6

Crystallographic summary for *fac*-[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$·H$_2$O, **5** [a]

Crystal data		
Formula:	$C_{33}H_{32}F_3MnO_8P_2S$	
Color and habit:	Light yellow prisms	
Size (mm):	0.45×0.50×0.50	
Crystal System:	Triclinic	
Space group:	$P\bar{1}$ (No. 2)	
Unit cell dimensions:	a = 11.782(2)	α = 95.27(1)
(a,b,c in Å)	b = 12.031(2)	β = 89.30(1)
(angles in °)	c = 13.720(2)	γ = 111.68(1)
Volume (Å^3):	1799.1(4)	
Z (formulae/cell)	2	
Formula weight:	762.59	
Density, calc. (g/cc):	1.41	
Absorption coeff. (cm^{-1}):	5.55	
F(000) (e$^-$):	784	
Data collection		
Diffractometer:	Siemens $R3m$	
Radiation:	Mo-K_α (λ = 0.71073 Å)	
Monochromator:	Highly oriented graphite crystal	
Temperature (K):	294	
2θ range (°):	3.0 to 55.0	
h,k,l limits:	−15–15, −15–15, 0–17	
Scan type:	$2\theta-\theta$	
Scan speed (°/min):	Variable; 2.0 to 8.0	
Scan range (°):	0.8 on either side of $K_{\alpha_{12}}$	
Background measurement:	Stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5.	
Standard reflections:	3 measured every 37	
Reflections collected:	8660 total; 8312 independent; R_{int} = 0.0292	
Reflections observed:	5458; $F > 6\sigma(F)$	
Absorption correction:	Semi-empirical (XEMP)	
Min./Max. transmission:	0.6696/0.8330	
Solution and refinement		
System used:	Siemens SHELXTL PLUS (MicroVAX II)	
Solution:	Sharpened Patterson (XS: PATT)	
Refinement method:	Full-matrix least-squares (XLS)	
Absolute configuration:	N/A	
Extinction correction:	N/A	
Final residuals:	$R(F)$ = 0.0665	$R_w(F)$ = 0.0956
Goodness-of-fit:	S = 1.69	
Max. and mean |Shift/ESD|:	0.001 and 0.000	
Number of variables:	439	
Data-to-parameter ratio:	12.4:1	
Max./min. excursions:	0.75 and −0.54 e$^-$/Å^3	

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[a] $R(F)=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, $R_w(F)=[\Sigma(w\|F_o|-|F_c\|^2)/\Sigma w|F_o|^2]^{1/2}$, $w=[\sigma^2(F)+|g|F^2]^{-1}$ $S=[\Sigma(w\|F_o|-|F_c\|^2)/(M-N)]^{1/2}$, where M is the number of observed reflections, and N is the number of parameters refined.

Preparation of the hydroxycarbene 5

To 0.600 g (1 mmol) of the acyl complex **4** was added 15 mL $CHCl_3$. To the resulting yellow solution was added by syringe, 110 μL (1.24 mmol) of neat triflic acid. The solution turned a deep yellow color immediately. Pentane (35 mL) was added and the two phase mixture cooled in the refrigerator. The lemon yellow crystals which precipitated were filtered and air dried, 0.669 g (87%); m.p. 127–130 ° C with decomposition. IR (CH_2Cl_2): ν(C=O) 2026 (s), 1967 (s), 1955 (s) cm^{-1}; ν(C–F) 1232 (s), 1206 (s) cm^{-1}; ν(S=O) 1176 (m), 1015 (m) cm^{-1} (see ref. 8).

X-ray analysis of fac-*[(DPPP)(CO)$_3$Mn=C(OH)CH$_3$]SO$_3$CF$_3$ · H$_2$O, 5*

Suitable single crystals of **5** were obtained by crystallization from $CHCl_3$/pentane at −5 ° C. Crystal data, collection parameters, and solution and refinement information are summarized in Table 6. The structure was solved by heavy-atom methods (XS : PATT) in the triclinic space group $P\bar{1}$ (No. 2), and refined by full-matrix least-squares employing a weighing scheme based on $\sigma(F)$, anisotropic temperature parameters for the non-hydrogen atoms and fixed isotropic values of U(H) = 0.08 for the H atoms [21]. The methyl substituent was treated as a rigid group, while all other carbon-bound H atoms were placed at idealized positions. The coordinates of the hydroxy hydrogen atom were taken from a difference-Fourier map and were free to vary. The triflate anion exhibited large thermal vibrations and all attempts to fit it with a variety of partially occupied disorder models were poorly behaved. Consequently, the atoms of the triflate anion were assigned whole occupancies and refined anisotropically. The H atoms of the water of crystallization were not visible in any of the difference-Fourier maps and were not included. This water was probably picked up adventiously from the atmosphere by the very hygroscopic triflic acid. The final residuals were $R(F) = 0.0665$ and $R_w(F) = 0.0956$, and the goodness-of-fit was $S = 1.69$.

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