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Synthesis And Structural Characterization of A Stable Hydroxycarbene

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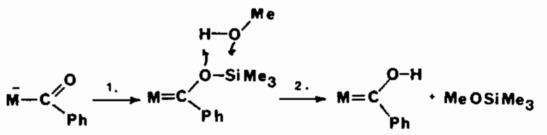
Hydroxycarbenes, which are frequently obtained by direct protonation of anionic metal carbonyl acylates/benzoylates, very readily decompose to yield aldehydes [1, 2] and only a few hydroxycarbenes have been found to be reasonably stable at room temperature [3–5]. In this paper we report the synthesis of thermally stable hydroxycarbenes of molybdenum and tungsten and the characterization of one of them by a single crystal X-ray diffraction study – the *first of a hydroxy carbene.*

The molecules *1* containing a 13-crown-4-ether ring will react with RLi to give the stable acylate/benzoylates *2* [6]. The formation of *2* is a direct consequence of strong lithium ion binding in the cavity defined by the acylate/benzoylate and crown ether oxygens [6–8]. Reaction of *2* with a molar equivalent of Me_3SiCl followed by MeOH or aqueous hydrolysis and subsequent work up leads to the formation of the very stable hydroxycarbenes *3* isolated as deep red-purple crystalline solids (60–80% yields). See Table I for physical and spectroscopic properties. The reaction probably proceeds as outlined in eqn. 1.



(1)

Because of our interest in metal carbonyl/crown ether systems and the lack of any previous structural studies of a hydroxycarbene we have determined the structure of *3a* by X-ray diffraction.

Crystal Data

Complex *3a*, $C_{40}H_{38}O_8P_2Mo$, M = 804.63, Monoclinic, space group $P2_1/n$, a = 17.266(3), b = 17.785(3), c = 12.158(2) Å, β = 91.62(2)°. Cell voume 3731.9 Å^3, Dc 1.432 g cm^{-3}, $Z = 4$, μ(MoK$\bar{\alpha}$) 4.76 cm^{-1}.

TABLE I. Physical and Spectroscopic Data.

Complex	mp °C	Analysis: Calcd. (Found)			Ir(νCO) cm^{-1}	δ ^{31}P ppm	^{1}H NMR data (CH_2Cl_2)
		C	H	P			
3a	125–126	59.71(59.69)	4.76(4.77)	7.70(7.55)	1953s, 1863sb	142.9	δ3.5–3.8(m, 12H) ring; δ7.1–7.6(m, 25H) Ph's; δ14.2 ppm (t, 1H) *OH* $J_{^{31}P-H}$ ~ 1.5Hz; D_2O exchangeable
3b	129–131	53.83(54.82)	4.29(4.56)	6.94(6.88)	1952s, 1870sb	122.9 J_{WP} 272 Hz	δ3.6–3.8(m, 12H) ring; δ7.1–7.6(m, 25H) Ph's; δ13.8(t, 1H) *OH* $J_{^{31}P-H}$ ~ 1 Hz; P_2O exchangeable

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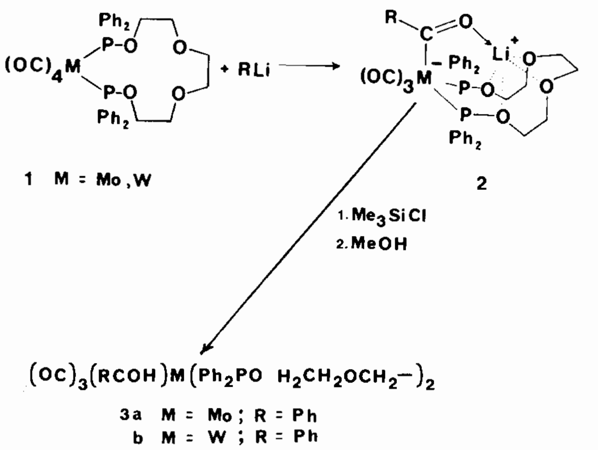
TABLE II. Selected Bond Distances and Angles.

Bond	Distance (A)	Bond	Distance (A)
Mo–P(1)	2.496(2)	P(1)–C(21)	1.819(6)
Mo–P(2)	2.485(2)	P(1)–C(31)	1.824(6)
Mo–C(1)	2.172(6)	P(2)–C(41)	1.834(6)
Mo–C(2)	2.000(7)	P(2)–C(51)	1.813(6)
Mo–C(3)	1.968(7)	P(1)–O(5)	1.630(4)
Mo–C(4)	1.968(7)	P(2)–O(8)	1.625(4)
		O(5)–C(5)	1.453(7)
C(1)–O(1)	1.333(7)	C(5)–C(6)	1.493(9)
C(1)–C(11)	1.497(8)	C(6)–O(6)	1.407(8)
		O(6)–C(7)	1.412(8)
C(2)–O(2)	1.144(7)	C(7)–C(8)	1.502(11)
C(3)–O(3)	1.171(7)	C(8)–O(7)	1.400(10)
C(4)–O(4)	1.158(7)	O(7)–C(9)	1.411(9)
		C(9)–C(10)	1.456(12)
		C(10)–O(8)	1.427(8)
Atoms	Angle (deg)	Atoms	Angle (deg)
P(1)–Mo–P(2)	90.85(5)	P(1)–O(5)–C(5)	123.6(4)
P(1)–Mo–C(1)	88.8(2)	O(5)–C(5)–C(6)	107.0(5)
P(2)–Mo–C(1)	88.7(2)	C(5)–C(6)–O(6)	108.1(5)
C(1)–Mo–C(2)	175.5(2)	C(6)–O(6)–C(7)	115.8(5)
P(1)–Mo–C(2)	91.0(2)	O(6)–C(7)–C(8)	111.8(6)
P(2)–Mo–C(2)	86.9(2)	C(7)–C(8)–O(7)	109.9(6)
C(3)–Mo–C(4)	88.4(2)	C(8)–O(7)–C(9)	116.3(7)
		C(7)–C(9)–C(10)	110.0(6)
Mo–C(1)–O(1)	124.0(4)	C(9)–C(10)–O(8)	110.2(7)
Mo–C(1)–C(11)	128.1(5)	C(10)–O(8)–P(2)	126.0(4)
C(11)–C(1)–O(1)	107.8(5)		
Mo–C(2)–O(2)	178.0(5)		
Mo–C(3)–O(3)	175.9(5)		
Mo–C(4)–O(4)	177.4(6)		



Purple crystals of $(OC)_3(PhCOH)Mo(Ph_2POCH_2CH_2OCH_2-)_2$ were obtained by recrystallisation from acetone. X-ray diffraction measurements were made with an Enraf-Nonius CAD4 diffractometer. Three standard reflections, monitored every 2.8 hours during data collection, showed no decomposition had occurred. A total of 6324 reflections was measured. The recorded intensities were corrected for Lorentz and polarization effects and a standard deviation $\sigma(I)$ was assigned to each intensity (I), using the data reduction programme of the Enraf-Nonius SDP system. Of the total reflections processed, 3310 unique data with $I > 3\sigma(I)$ were used in the solution and refinement of the structure.

The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques on F. Scattering factors for the atoms were taken from Volume IV [9]. The correction for anomalous dispersion was included for the Mo and P atoms. In the final cycles phenyl and methylene hydrogen atoms were placed in calculated positions (Csp^2–H = 0.95 Å, Csp^3–H = 1.0 Å) with fixed temperature factors B = 5.0 Å^2 but were not refined. The refinement of 310 variables with 3310 observations ($I > 3\sigma(I)$), converged at agreement factors R = 0.0525 and Rw = 0.0664 (maximum shift error = 0.06). The function minimized was

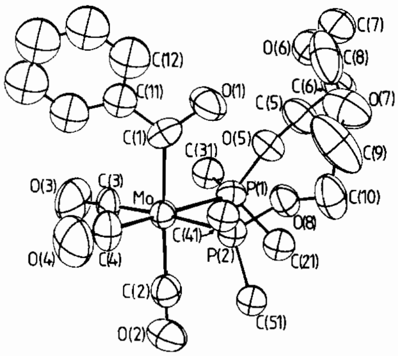


Fig. 1. An ORTEP drawing of the complex $[(OC)_3(PhCOH)Mo(Ph_2POCH_2CH_2OCH_2-)_2]$ with 50% probability ellipsoids. Only the α-C atoms of the diphosphinite phenyl rings are shown.

$\Sigma\omega||Fo| - |Fc||^2$ where the weight ω is given by $4Fo^2/(\sigma(I)^2 + (pI)^2)$; p was chosen as 0.05. The error of an observation of unit weight was 1.60 electrons. In the final difference Fourier synthesis, the highest peak is of electron density 0.62 $e\text{Å}^{-3}$ and is of no chemical significance.

Selected bond lengths and bond angles for the complex are given in Table II. A perspective view of the molecule showing the atom numbering scheme is presented in Fig. 1. Only the α-carbon atoms of the diphosphinite phenyl rings are shown. The coordination geometry about the metal is approximately octahedral and three of the six coordination sites are occupied by carbonyl ligands in a *fac* arrangement. The three remaining sites contain a diphosphinite ligand and a phenylhydroxycarbene ligand. The two Mo–P distances are 2.496(2) and 2.485(2) Å. The dimensions associated with the diphosphinite ligand are normal [6]. The ligand has a similar though by no means identical conformation in the carbene complex, to that observed in the Li salt *2a.* The Mo–C (carbonyl) bond length *trans* to the P atoms are identical, 1.968(7) Å, and slightly longer (3.2σ) than the Mo–C(2) distance *trans* to the carbene ligand, 2.000(7) Å [9]. The Mo–C(1) (carbene) distance of 2.172(6) Å is significantly longer than those to the carbonyl ligands but is approximately 0.2 Å shorter than that expected for a Mo–C(sp^2) single bond [6]. A value of 2.25 Å was found for *2a* [6] and 2.15(2) Å for the carbene complex $Mo(CO)_5\{C(OEt)(SiPh_3)\}$ [10].

The dimensions associated with the phenylhydroxy carbene ligand are consistent with its formulation. While the H bonded to O(1) could not accurately be located, there is a 'smear' of positive electron density in the region between O(1) and O(5). The distance between O(1) and O(5), is 2.686(6) Å, compared with a value of 3.233(6) Å to O(8). The corresponding distances to O(6) and O(7) are 3.265(7) and 3.671(7) Å. This suggests that the OH group is stabilised in the complex by hydrogen-bonding to O(5) of the diphosphinite backbone. The O(1)••••O(5) distance lies within the range of values found in hydrogen-bonded systems [11]. In addition, the C(1)–O(1) bond length of 1.333(7) Å is indistinguishable from the distance 1.35(2) Å found in the carbene complex $Mo(CO)_5\{C(OEt)(SiPh_3)\}$ [10] and significantly longer than the C=O bond length reported for *2a* of 1.26 Å [5].

The geometry about the C(1) atom is approximately trigonal planar. Whilst metal carbonyl acylates/benzoylates are destabilised by increased tertiary phosphine substitution (*e.g.* *cis*-$(OC)_4M(PR_3)_2$ complexes are generally unreactive towards RLi addition [6]) the corresponding carbenes (*e.g. 3*) are stabilised. This is probably due to the increased basicity of the metal centre which results in an increase in the double bond character of the M–carbene bond. Also the presence of a strong intramolecular hydrogen bond between the hydroxycarbene and an adjacent ligand as in *3a* may be a significant factor in stabilizing these species. Spectroscopic studies of other isolable hydroxycarbenes of Mn and Re indicate the presence of intramolecular hydrogen bonds [3–5].

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