$\overline{C_6H_4}CH)]_2O$ (**5**) was isolated (28–36%).[11b] Under slightly different conditions, CF_3SO_3H (0.21 equiv, benzene) effected hydride transfer disproportionation of **4** to the cyclometalated acyl $(CO)_4\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4C}{=}O)$ (**6**, 0.40 equiv) and alkyl $(CO_4)\overline{ReP(C_6H_5)_2(o\text{-}C_6H_4CH_2})$ (**7**, 0.37 equiv).[16] Similar acid promoted conversion of the α-hydroxyalkyl $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2OH)$ to a symmetrical ether has been previously observed by Casey,[8b] and we have noted a related electrophile-induced hydride transfer disproportionation of the methoxyalkyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$.[17] Interestingly, workup of the reaction of **3** with $(C_2H_5)_4N^+F^-\cdot(H_2O)_x$ (ca. 0.95 equiv) prior to silica gel filtration afforded the crystalline, fac-substituted anionic tricarbonyl **8** in 93% yield (Scheme I).[11b]

Subsequent to the above isolation of **4**, we were able to detect minor amounts by TLC in other attempted syntheses. By careful optimization of conditions, we obtained **4** in 72% yield by reduction (Scheme II) of **6** with $BH_3\cdot THF$ (2 equiv). Although BH_3 has been previously noted to convert acyl ligands to alkyl ligands,[18] this is the first time that partial reduction of an acyl ligand has been observed.

Efforts to prepare **4** by routes analogous to the reverse of eq 1 were not successful. Substitution of CO in $(CO)_5ReH$ by phosphines is known to occur at erratic rates by free radical chain mechanisms;[19] tractable products did not result from the reaction of $(CO)_5ReH$ with $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$.[12] $(CO)_4LReH$ complexes were obtained from the reactions of $(CO)_5ReH$ with $(C_6H_5)_2P(o\text{-}C_6H_4\overline{CHOCH_2CH_2O})$ and $(C_6H_5)_2P[o\text{-}C_6H_4CH(OCH_3)_2]$. However, we were not able to deprotect the aldehyde functionality once these phosphines were coordinated. Recourse was then made to the more acidic and substitution-labile hydride $(CO)_5MnH$.[19,20] Gratifyingly, its reaction with $(C_6H_5)_2P(o\text{-}C_6H_4CHO)$ gave the manganese α-hydroxyalkyl **9** (Scheme III) in quantitative spectroscopic yield over the course of 8 h at 25 °C.[11b] After column chromatography, **9** was obtained as a stable light yellow powder in 70% yield; spectral properties were very similar to those of **4**.[11b]

The above data, together with our interpretation of the factors contributing to the stability of previously isolated α-hydroxyalkyl complexes, indicate a substantial analogy of organometallic $L_nMCH(R)OH$ with organic $XCH(R)OH$ systems. Hence when the metal is "electron rich" (3rd-row metal and good donor lignds; strategy a), the α-hydroxyalkyl complex is more stable; other thermal reactions may be able to compete with eq 1 type aldehyde extrusion. Furthermore, since the corresponding metal hydride would not be very acidic,[20] such α-hydroxyalkyls should not be kinetically accessible (or only with great difficulty) from aldehydes and L_nMH; rather, alkoxide formation might be the preferred reaction course.[21] First-row transition-metal hydrides tend to be more acidic,[20] but they are also less electron rich. Hence they may react with aldehydes to give small equilibrium quantities of α-hydroxyalkyls (which can be trapped or react further),[7] but strategies b or c must be utilized to obtain isolable species.

The foregoing generalizations should apply equally well to homogeneous catalytic systems and may provide significant insight into catalyst design. Additional properties of the new compounds reported herein will be described in due course.

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Supplementary Material Available: Characterization of **2–5**, **8**, **9** (3 pages). Ordering information is given on any current masthead page.

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(16) Compound **6** has been prepared previously.[13] An authentic sample of **7** was synthesized from commercially available $(C_6H_5)_2P(o\text{-}C_6H_4CH_3)$ using procedures similar to those employed by Kaesz and McKinney for the cyclometalation of $P(o\text{-}C_6H_4CH_3)_3$.[13]

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Efficient and Accurate Calculation of Anion Proton Affinities

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Theoretical investigations of anionic species pose special problems.[1] Since the electron affinities of the corresponding neutral species are often quite low,[2] the extra electron in the anion is only weakly bound. With commonly employed ab initio methods, the HOMO's of anions are often indicated erroneously to have positive energies, i.e., to be unbound.[1] Absurdly negative values for electron affinities are often calculated, especially when electron correlation is not taken into account. Even protonation energies (for which single determinant theory is more appropriate due to conservation of electron pairs) are not predicted well for anions by methods which perform adequately for neutral and positively charged systems.[3] Minimal basis sets, even with "anion optimized" exponents,[4] and double-zeta or split-valence basis sets[5] yield proton affinities (PA's) with unacceptably large errors. These deficiencies are exemplified by the collection of PA data in Table I for a representative set of 19 closed-shell first-row anions. Errors with the STO-3G basis (standard exponents) are 110–230 kcal/mol; the split-valence 4-31G basis set PA's on the average are 31 kcal/mol greater than the experimental values.[2] No significant overall improvement is achieved either by inclusion of polarization functions (d orbitals) in the basis set, e.g., 6-31G*//4-31G, or by correcting for electron correlation, e.g., MP2/6-31G*//4-31G (Table I).[6g] Radom's conclusion, that "near-Hartree-Fock basis sets may be required to provide accurate absolute values of proton affinities",[1a] is discouraging. Consequently, most general theoretical studies on anions have been confined to more limited goals, viz., to obtain structural information[1a,6b] or evaluate stabilization energies through the use of

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Table I. Comparison of Calculated with Experimental Proton Affinities of Anions (kcal/mol)

anion	STO-3G// STO-3G[a]	4-31G// 4-31G[b]	6-31G*// 4-31G[b]	MP2/6-31G*// 4-31G[b]	4-31 + G// 4-31+G[c]	MP2/4-31 + G// 4-31+G[c]	exptl[d]	MNDO[e]	best previous calculation[f]
H^-	601.7	442.0[c]	442.0[c]	448.8[c]	401.8	404.8	400.4		405.0[r]
CH_3^-	559.8	463.1	457.3	458.1	433.5	425.2	416.6	435.7	425.2[g]
NH_2^-	547.0	448.6[h]	444.7[c]	445.9[c]	421.2	408.7	403.6	420.6	422.0[s]
OH^-	565.3	426.0[h]	429.3[i]	428.7[i]	394.6	381.1	390.8	422.1	403.2
F^-	602.1	401.3[h]	409.4[c]	411.4[c]	361.9	351.3	371.5	411.3	379.1[r]
$C_2H_5^-$		461.0	455.9	454.1	439.1	432.0		414.1	432.3[g]
$C_2H_3^-$	527.7[j]	444.7[k]			423.8	417.9	>404	421.1	438.4[l]
C_2H^-	496.4	408.3[k,m]			385.6	383.1	375.4	413.9	391.6
CN^-	462.8	374.2[m]	369.9[i]		354.2	353.7	353.1	387.0	352.0
CH_3NH^-	529.0[h]	440.3[h]			422.6	410.7	403.2	398.0	440.3[h]
CH_3O^-	528.9	409.8[h]			393.1	381.4	379.2	384.6	409.8[h]
$CH_3C{\equiv}C^-$	499.9[n]	414.1[n]			393.2		379.6	407.2	409.3[k]
allenyl$^-$	513.4	419.0	414.4	411.5	400.0			392.2	407.4[o]
allyl$^-$	515.8[p]	425.7	425.4	420.9	405.5	399.1	387.2	388.1	412.0[o]
CH_2CHO^-	503.0	391.6	396.8	391.9	374.5	369.2	366.4	373.4	381.3[o]
$CH_3CH_2O^-$	534.2[q]	409.7[q]			391.7	378.7	376.1	384.7	409.7[q]
CH_2CN^-		402.0	402.2	400.2	386.1	383.4	372.2	390.7	391.3[o]
$HCOO^-$		359.9[n]			346.9	337.3	345.2	358.0	333.4
$CH_2NO_2^-$	469.5[h]	365.0	381.4		350.5		358.7	355.4	355.0[o]

[a] Unless otherwise noted, calculated from data in: Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University; Pittsburgh, PA, 1980. [b] Unless otherwise noted, ref 6g. [c] This work. [d] Reference 2b. [e] This work, except for data taken from ref 12 and 13. [f] Unless otherwise indicated, data from ref 1a,b and 5a. [g] Reference 8i. [h] Reference 6d. [i] 6-31G*//6-31G*, footnote a. [j] Reference 15b. [k] Reference 5a. [l] Reference 4. [m] Reference 5c. [n] Reference 6a. [o] Reference 7a. [p] Reference 5b. [q] Standard geometry for the anion, ref 6b. [r] Reference 8s. [s] Reference 8t.

isodesmic reactions[1,4-7] (cancellation of errors is assumed, but this does not always occur).

A possible way to overcome such problems with anion calculations has been long known and is widely appreciated.[8] Systems with weakly bound HOMO's are not adequately described by basis sets appropriate for neutrals and positive ions. Diffuse functions are essential for a proper description of the tail behavior of MO's with energies close to the ionization limit.[8] Such functions have dramatic effects on calculated electron affinities,[8e] inversion barriers,[8a,c] and proton affinities.[8i] Kollmar found that an SCF calculation with a double-zeta basis including one set of diffuse functions was as good as the result of a correlation-corrected (CEPA) calculation with a very extended basis in predicting the proton affinity of the methyl anion.[8i] There was a 1000-fold difference in computer time between these two calculations! Despite these promising results, general studies of anions with basis sets including diffuse functions have not been reported, and numerous recent theoretical investigations of anions have not employed diffuse-orbital augmented basis sets.[6,7] We have now evaluated the performance of various theoretical levels in reproducing experimental results.

Our objective is the efficient calculation of anion proton affinities rather than the inherently more difficult estimation of electron affinities. Following Kollmar's lead[8i] and Radom's finding that the 4-31G basis reproduces experimental anion geometries satisfactorily,[1a,6b] we developed a diffuse function augmented 4-31+G basis set by adding a set of flat s and p functions to all first-row atoms, Li–F. The optimized exponents for these functions were obtained at the 6-31G level for the anions indicated: F^-, 0.090; OH^-, 0.068; NH_2^-, 0.053; CH_3^-, 0.040; BH_2^-, 0.034; BeH^-, 0.026; Li^-, 0.012.[9] We also tested the addition of diffuse functions to hydrogen. This improved the calculated PA's somewhat, but at the expense of more computer time and greater problems with convergence. Hence, the 4-31+G basis does not include any additional hydrogen functions. (However, a diffuse s function (exponent = 0.036) is needed to describe H^- satisfactorily.)

Complete geometry optimization (4-31+G//4-31+G) for the representative set of anions (Tables I and II) was carried out by using analytically evaluated gradients.[10] These geometries were employed in second-order Møller–Plesset correlation correction calculations (MP2/4-31+G//4-31+G).[11] At these levels, the HOMO's of all anions reported in Table I are negative, but this may be misleading. Thus, MP2/4-31+G calculations are not adequate to estimate electron affinities directly. For example, the energy of $CH_3\cdot$ (UMP2/4-31+G//UHF/4-31+G) is lower than that of CH_3^- (the experimental EA of $CH_3\cdot$ is only 1.8 kcal/mol).[2] However, EA's can be estimated indirectly by appropriate isodesmic equations or thermochemical cycles if data for the corresponding radicals are available. Since Dewar and Rzepa found that experimental electron affinities are reproduced reasonably well by MNDO[12] (with some exceptions),[13] we included calculations for anions at this semiempirical level in Table I for comparison.

The 4-31+G proton affinities (Table I), already in agreement with the experimental results (average deviation = 10 kcal/mol), are even better when corrected to 298 K by estimating the zero-point vibrational and the rotational and translational contributions. These corrections usually will decrease the calculated values, e.g., by -5.4 (H^-), -8 (CH_3^-),[8i] - 7.3 (NH_2^-), -6.2 (OH^-), -4.8 (F^-), and +0.4 (CN^-) kcal/mol.[1b] The MP2 electron cor-

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Table II. Calculated Energies of Anions[a]

anion	MNDO ΔH_f°	4-31+G//4-31+G		MP2/4-31+G//4-31+G	
		E	rel E	E	rel E
CH_3^- C_{3v}		−39.45004	0.0	−39.56471	0.0
D_{3h}	56.8	−39.44925	0.5	−39.56240	1.5
NH_2^-	47.3	−55.44372		−55.58263	
OH^-	−5.8	−75.29023		−75.44611	
F^-	−15.5	−99.32621		−99.48112	
HCC^-	104.3	−76.10407		−76.29182	
CN^-	54.9	−92.17341		−92.38787	
$C_2H_3^-$, C_s		−77.25246	0.0	−77.44387	0.0
C_{2v}	71.0	−77.20437	30.2	−77.39999	27.5
$CH_3CH_2^-$, staggered		−78.41769	0.0	−78.62297	0.0
eclipsed		−78.41444	2.0	−78.61975	2.0
bisected	27.3	−78.41328	2.7	−78.61923	2.3
CH_3NH^-, staggered	23.5	−94.40502		−94.63251	
CH_3O^-	−39.8	−114.25329		−114.49415	
1-cyclopropenyl	109.6	−115.01329	−40.7	−115.29720	−38.3
2-cyclopropenyl, C_s[b]	135.0	−114.94839	0.0	−115.23610	0.0
C_{2v} (I)[b]		−114.89163	35.6	−115.17982	35.4
C_{2v} (II)[c]		−114.89649	32.6	−115.19008	28.9
cyclopropyl, C_s		−116.19378	0.0	−116.48368	0.0
C_{2v}	56.9	−116.16647	17.1	−116.45966	15.1
allyl, C_{2v}	26.0	−116.26470	0.0	−116.54910	0.0
C_s, perp (I)[d]	50.0	−116.22464	25.1	−116.51378	22.2
C_s, perp (II)[e]	50.0	−116.22270	20.4	−116.51155	23.6
HCO_2^-	−101.7	−187.93281		−188.29722	
$C_2H_5O^-$	−45.3	−153.24029		−153.57512	
CH_2CN^-	31.7	−131.11943		−131.42397	
CH_2CHO^-, planar	−36.0	−152.09574	0.0	−152.41991	0.0
perp	9.4	−152.03117	40.5	−152.35635	39.9
$CH_2NO_2^-$, planar	−14.9	−242.73224	0.0		
perp		−242.66192	44.1		

[a] Total energies in hartrees; relative energies and MNDO heats of formation in kcal/mol. [b] En-yl form. [c] Allyl form. [d] Carbanion lone pair anti to the double bond. [e] Carbanion lone pair syn to the double bond.

relation corrections, though only modest, result in further improvement (MP2/4-31+G//4-31+G, Table I). The accuracies of our calculated proton affinities are as good as or are superior to the best literature ab initio values (Table I, last column). MNDO proton affinities are also often quite satisfactory (the electron correlation and zero-point corrections are included in the MNDO parametrization), but smaller anions, in which the charge is concentrated on one atom, show larger deviations. Similar behavior was noted in the calculated MNDO electron affinities.[13] The average error for the anions in Table I, 14 kcal/mol, is much lower than that at 4-31G//4-31G. However, the ordering of some of the PA's, e.g., CH_3O^- and $C_2H_5O^-$, is not given correctly by MNDO. MNDO geometries also have deficiencies; CC bonds are too short, CH bonds too long, and carbanion centers too flat. Nevertheless, the speed and reasonable accuracy of MNDO facilitate the study of larger anions.

The 4-31+G geometries (available in the Supplementary Material) are only slightly different from those at 4-31G.[1a,5-7] Thus, computer time can be saved and little accuracy lost by using 4-31G geometries for single-point 4-31+G//4-31G calculations. The more efficient 3-21G basis set[14] can also be used for anion geometry optimizations.

The results for a large number of negatively charged species, including all C_3 and C_4 carbanions, will be presented subsequently.[20] We note here that the MP2/4-31+G inversion barriers for CH_3^- (1.5 kcal/mol) and $C_2H_5^-$ (2.3 kcal/mol) (Table II) are in good agreement with higher level calculations.[8a,c,i] The inversion barrier of $C_2H_3^-$ (27.5) and the rotational barrier of the allyl anion (22.2) are lower than previous estimates (34–50 for $C_2H_3^-$,[4,8j,15] 26 for the allyl anion[16]). The inversion barrier in the cyclopropyl anion is 15 kcal/mol; that in the antiaromatic 3-cyclopropenyl anion is even larger, 35 kcal/mol. These values are in qualitative agreement with previous calculations,[17] but are substantially lower. The MP2/4-31+G hydrogenation energies of 3-cyclopropenyl anion (−64.9) and cyclopropene (−61.4) lead to a resonance energy of only −3.5 kcal/mol (destabilization) for the cyclopropenyl anion.[18] Similar procedures yield resonance stabilization energies of 15 kcal/mol for the cyclopropenyl radical[19] and 70 kcal/mol for the cyclopropenium ion.[20] Most of the antiaromatic destabilization in the 3-cyclopropenyl anion is removed by the out-of-plane bending of the hydrogen at the anionic center. The 1-cyclopropenyl carbanion, however, is much more stable.

Diffuse function augmented split-valence basis sets of relatively modest size, such as 4-31+G or 3-21+G,[21] give reasonably reliable proton affinities of anions. We have evaluated the performance of larger basis sets, but more accurate PA's are obtained only in a few instances. MP2/4-31+G electron correlation corrections provide further improvement. We have now employed these levels of theory widely[22] and feel they can be recommended for sys-

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tematic investigations of anions.

Note Added in Proof: The rotational barriers in the anions from acetaldehyde, CH_2CHO^-, and from nitromethane, $CH_2NO_2^-$, are large, 40 and 44 kcal/mol, respectively. The calculated proton affinities of F^- and OH^- are improved when d orbitals as well as diffuse functions are included in the basis set. The PA's are, respectively, 373.6 and 401.1 kcal/mol at 6-31+G*/4-31+G and 387.1 and 362.0 kcal/mol at MP2/6-31+G*//4-31+G. We thank G. W. Spitznagel and T. Clark for this data.

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Supplementary Material Available: Calculated geometries (Table 3) and energies of neutral molecules (Table 4) (4 pages). Ordering information is given on any current masthead page.

Thermodynamic Stability of Carbonyl Anions, $\mathrm{R{-}C^{-}{=}O}$. A Molecular Orbital Examination

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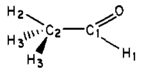
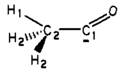
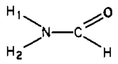
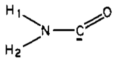
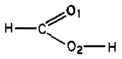
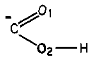
Carbonyl anions, $\mathrm{R\text{-}\bar{C}{=}O}$ (**1**), are generally inaccessible as practical synthetic intermediates. Consequently, many carbonyl anion "synthons" have been devised in order to achieve indirectly transformations like eq 1.[1] Carbonyl anions (as metalated de-

$$\underset{\mathbf{1}}{\mathrm{R\text{-}C^{-}{=}O}} + \mathrm{R'X} \rightarrow \mathrm{RR'C{=}O} + \mathrm{X^-} \qquad (1)$$

rivatives) are involved in the reaction of carbon monoxide with organolithium and Grignard reagents, but the variety of products often obtained indicate the high reactivity and kinetic instability to be expected of RCOLi or RCOMgX species.[2] There is evidence for the transient formation of C^-OOR and C^-ONR_2 in solution,[3] $LiCONR_2$ and $LiCONRNR'_2$ reagents are useful synthetically.[4] In the gas phase, $ClCO^-$ dissociates readily into CO and Cl^-,[5] reactions of various bases (B^-) with formate esters, which might have given (C^-OOR, led to $ROHB^-$ and CO instead,[6] and the formyl anion, HCO^-, can be observed,[7] but appears to be only marginally stable toward both electron and CO loss (see below). The benzoyl anion, $C_6H_5CO^-$, has been generated in the gas phase recently,[8] and proton abstraction from $CH_2{=}CHCHO$[9] as well as from $(CH_3)_3CCHO$[10] has been investigated.

Table I. 4-31+G Calculated Geometries of Carbonyl Systems[a]

HCO^-	CO = 1.254; CH = 1.166; ∠HCO = 110.0
H_2CO	CO = 1.209; CH = 1.080; ∠HCO = 121.6
	CC = 1.493; CO = 1.212; C_2H_2 = 1.079; C_2H_3 = 1.085; C_1H_1 = 1.084; ∠CCO = 124.2; ∠$C_1C_2H_2$ = 110.6; ∠$C_1C_2H_{33}$ = 125.4;[b] ∠$H_3C_2H_3$ = 107.2; ∠$C_2C_1H_1$ = 116.3
	CC = 1.574; CO = 1.250; C_2H_1 = 1.093; C_2H_2 = 1.088; ∠CCO = 113.1; ∠$C_1C_2H_1$ = 112.2; ∠$C_1C_2H_{22}$ = 122.5;[b] ∠$H_2C_2H_2$ = 107.5
	CO = 1.219; CN = 1.346; CH = 1.080; NH_1 = 0.993; NH_2 = 0.990; ∠NCO = 124.6; ∠OCH = 121.3; ∠CNH_1 = 119.7; ∠CNH_2 = 121.8
	CO = 1.261; CN = 1.414; NH_1 = 1.003; NH_2 = 0.989; ∠NCO = 113.0; ∠CNH_1 = 120.8; ∠CNH_2 = 119.8
	CO_1 = 1.203; CO_2 = 1.341; CH = 1.071; OH = 0.957; ∠HCO_1 = 125.1; ∠CO_2H = 115.2; ∠HCO_2 = 110.7
	CO_1 = 1.235; CO_2 = 1.484; OH = 0.964; ∠OCO = 110.3; ∠COH = 110.0
FCHO	CF = 1.361; CO = 1.179; CH = 1.070; ∠FCO = 122.0; ∠HCO = 110.0
FCO^-	CF = 1.830; CO = 1.168; ∠FCO = 106.2

[a] Bond lengths in Å, angles in deg. See footnote 18. [b] CH_{aa} denotes the bisector of H_aCH_a angle.

Table II. Calculated Ab Initio Energies of Carbonyl Systems[a]

	4-31+G[b]		MP2/4-31+G//4-31+G[b]	
system	*E*	rel *E*	*E*	rel *E*
HCO^-	−113.05364		−113.27932	
H_2CO	−113.69766		−113.91974	
CH_3CHO	−152.69253		−153.00515	
CH_3CO^-	−152.04848	0.0	−152.37054	0.0
CH_2CHO^-	−152.09251	−27.6	−152.41432	−27.5
NH_2CHO	−168.69064		−169.02031	
NH_2CO^-	−168.05383	0.0	−168.39241	0.0
$NHCHO^-$	−168.09140	−23.6	−168.43674	−27.8
HCOOH	−188.48375		−188.82960	
$OCOH^-$	−187.87250	0.0	−188.22669	0.0
HCO_2^-	−187.92750	−34.5	−188.28706	−37.9
FCHO	−212.45367		−212.80355	
FCO^-	−211.88137		−212.24046	

[a] Total energies in hartrees, relative energies in kcal/mol. [b] Diffuse orbital exponents 0.04 added to *all* non-hydrogen atoms. See footnote 18.

To what extent are carbonyl anions *thermodynamically* unstable? The normal polarization of carbonyl groups (**2**) and the ease of formation and the thermodynamic stability of carbonyl

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