Lithium [Bis{benzoyl-W(CO)$_5$}(μ_2-hydrogen)] − A Charge-Assisted H$^+$-Bridged Organometallic Complex Prepared by Selective Li$^+$ Ion Replacement

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Dedicated to E. O. Fischer on the occasion of his 85th birthday

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Efficient syntheses and isolation procedures of two closely related benzoyl–W(CO)$_5$ compounds, [{Li(diglyme)}{Ph(O)-CW(CO)$_5$}] (**1**) and [Li(diglyme)$_2$][(μ_2-H){Ph(O)CW(CO)$_5$}$_2$] (**2**) are reported. The empirical formulae of **1** and **2** differ only in that the latter contains half the number of Li$^+$ ions, with the balance of cations replaced by protons through an acidic silica gel filtration procedure. X-ray structural investigations of both compounds revealed a self-assembled polymeric Li$^+$-bridged structure for **1**, and a strikingly dissimilar H$^+$-bridged structure for **2**, thereby emphasising the important influences of strong, charge-assisted hydrogen bonds on solid-state structures. Possible implications of this novel route to charge-assisted hydrogen bonds for crystal engineering are discussed.

Introduction

Hydrogen bonding effects are essential in crystal engineering.[1] Recent advances in organometallic crystal engineering, especially by the group of Braga and Grepioni, have exhibited the versatility of hydrogen bonds in the "construction" of extended organometallic structures.[2] Variation of the non-covalently bonded ligand components in the crystals may then ultimately enable chemists to "tune" the crystal so that aspects of transition metal coordination chemistry (e.g. variable valence, oxidation, and spin states of the metal atoms) are incorporated in the crystals.[2] Organometallic crystal engineering studies are presently focused mainly on the use of functionalised ferrocenes, and other sandwich compounds, in forming crystals with extended structures.[2] Carboxylic acid and 1,3-cyclohexanedione functionalities in these compounds are, furthermore, the preferred vehicles for introducing hydrogen bonds, which ultimately produce the extended structures of molecules in the crystals.[2] Strong, charge-assisted $O-H\cdots O^-$ hydrogen bonds − valuable tools for crystal engineers − are generally obtained by partial deprotonation of acidic moieties (typically carboxylic acids) in the crystals and significantly strengthen the extended structures.[3] These short hydrogen bonds, as they occur in homonuclear molecule−ion associates, AHA$^-$ (A = anion base, e.g. carboxylate anion), have been subject to intensive theoretical and experimental investigations and, also, much debate.[4]

Transition metal−acyl complexes are an extremely important class of organometallic compounds; they feature in many homogeneous catalytic processes, especially ones involving carbon monoxide,[5] and have hence been the subject of many reactivity and theoretical studies.[6] Transition metal−acyl complexes are also useful models for key catalytic intermediates in heterogeneous catalytic processes,[7] such as the Fischer−Tropsch process, where Fe-surface alkyl and acyl species play an important role in the formation of oxygenates (mainly formates, alcohols, and ketones).[8] Anionic transition metal−acyl complexes are, furthermore, important water-soluble intermediates in many synthetic routes to useful organometallic compounds, including Fischer's classical, and Semmelhack's more recent, methods to prepare carbene complexes.[9] Both routes involve the formation of anionic metal−acyl species that, upon oxygen alkylation/protonation, yield a wide variety of carbene complexes. Even though hydrogen bonding and cation coordination to metallo-acyl oxygen atoms in hydroxycarbene[10] and metal−acyl[11] complexes is well known, no examples of such complexes with extended solid state structures have been described.

We report here the isolation and structural characterisation of the widely employed organometallic reaction intermediate [Li(diglyme){Ph(O)CW(CO)$_5$}] (**1**), as a diglyme stabilised Li$^+$ salt, and the closely related H$^+$-bridged organometallic compound [Li(diglyme)$_2$][(μ_2-H){Ph(O)-CW(CO)$_5$}$_2$] (**2**) − both prepared from identical reaction mixtures. In the solid state, complex **1** exhibits a linear polymeric structure of Li$^+$-ion-bridged Ph(O)CW(CO)$_5$$^-$ ions

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in which the Li^+ ions coordinate to the acyl oxygen atom and a carbonyl oxygen atom of a neighbouring $Ph(O)CW(CO)_5^-$ ion. A strong, charge-assisted hydrogen bond in **2** bridges two $Ph(O)CW(CO)_5^-$ ions in the solid state structure. The remaining positive charge in **2** is provided by a Li^+ ion, indicating that only one Li^+ ion was selectively replaced during the filtration/protonation procedure executed on the common reaction mixture. In both compounds 1 mol equiv. of diglyme (diethylene glycol dimethyl ether) is incorporated to stabilise the Li^+ ion and it is, furthermore, thought to be imperative to the efficient selective protonation that affords **2**.

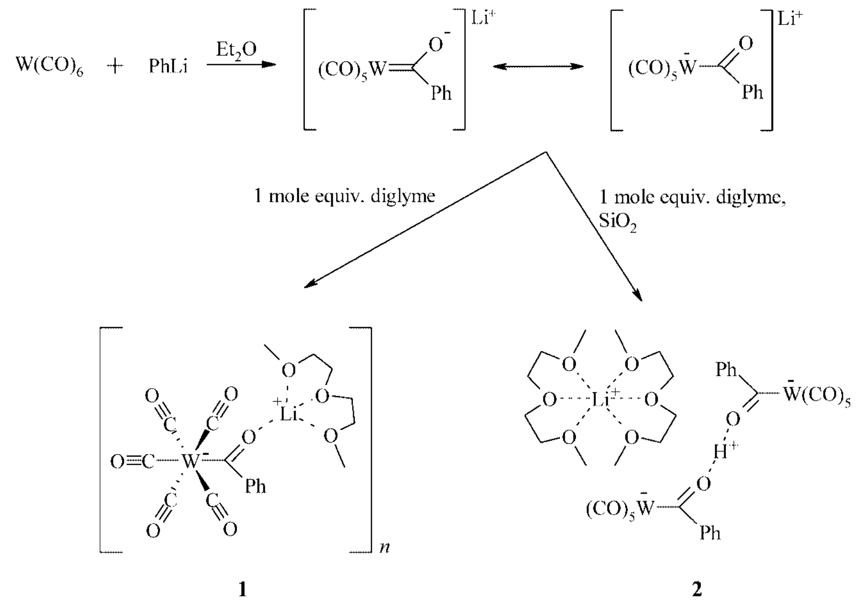
Results and Discussion

Synthesis and Isolation of Benzoyl−W(CO)$_5$ Complexes, Their Crystal Structures, IR Spectra, and NMR Spectra

The anionic benzoyl−$W(CO)_5$ complexes, **1** and **2**, were synthesized in the same manner as the first step of the synthesis of the Fischer-type carbene complex $[Ph(OR)C{=}W(CO)_5]$, i.e. by dropwise addition of 1.2 mol equiv. PhLi to a suspension of $W(CO)_6$ in Et_2O at room temperature.[9a] However, instead of alkylating the so-formed $Li[Ph(O)CW(CO)_5]$, **1** and **2** were prepared using slightly modified procedures (Scheme 1). Complex **1** was isolated in high yield [78%, based on $W(CO)_6$] as bright-red crystals, suitable for X-ray crystallographic analysis, by the addition of 1 mol equiv. diglyme to the reaction mixture and subsequent crystallisation from a diethyl ether/*n*-pentane mixture. Complex **2** was prepared similarly, except that the red reaction mixture was carefully filtered through cooled (0 °C) acidic silica gel (10−15 cm, Ø 4 cm) before crystallisation from a diethyl ether/*n*-pentane mixture to afford bright-red crystals of **2**, suitable for X-ray crystallographic analysis, in moderate yields [69%, based on $W(CO)_6$]. Et_2O was used to elute the mixture from which **2** crystallised as a slow-moving red band from the silica gel. This procedure is closely related to the synthesis of hydroxycarbene complexes, as originally reported by Fischer et al.[12]

Removal of half the Li^+ ions from the reaction mixture by proton exchange upon filtration through silica gel, so that **2** may crystallise, is closely linked to the amount of diglyme present in the reaction mixture. The Li^+ ions in the reaction mixture have to be strongly solvated to pass through the silica gel during the filtration procedure. As only one mol equivalent of diglyme is added to the reaction mixture, and two diglyme molecules are required to solvate each Li^+ ion (as in the crystal structure of **2**, Figure 3), exactly half the Li^+ ions remain in solution after chromatography. The other half are immobilised on the silica gel and, to balance the charge, are replaced by mobile protons. Et_2O solvent molecules do not solvate Li^+ ions strongly enough to facilitate their efficient mobilisation through silica gel.

Low-temperature crystal and molecular structures of **1** (173 K) and **2** (173 K) (Figure 1 and Figure 3) were determined by X-ray diffraction. The structure of **1** clearly shows a $Ph(O)CW(CO)_5^-$ ion interacting with a Li^+ ion through its acyl moiety. Li^+-coordination to the oxygen atom of the CO ligand *trans* to the benzoyl group [O(3)] in neighbouring anions results in infinite zig-zag chains of alternating $Ph(O)CW(CO)_5^-$ and Li^+ ions along the *a* axis of the unit cell of **1** (Figure 2). The remaining coordination positions on the Li^+ ion are occupied by a diglyme molecule, coordinating to the cation through all three of its ether oxygen atoms. The coordination mode of the five-coordinate Li^+ ion is best described as distorted square pyramidal, with O(3) at the apex. O(5) lies on the underside of the square pyramid, beyond bonding distance [O(5)−Li = 3.506(4) Å],



Scheme 1

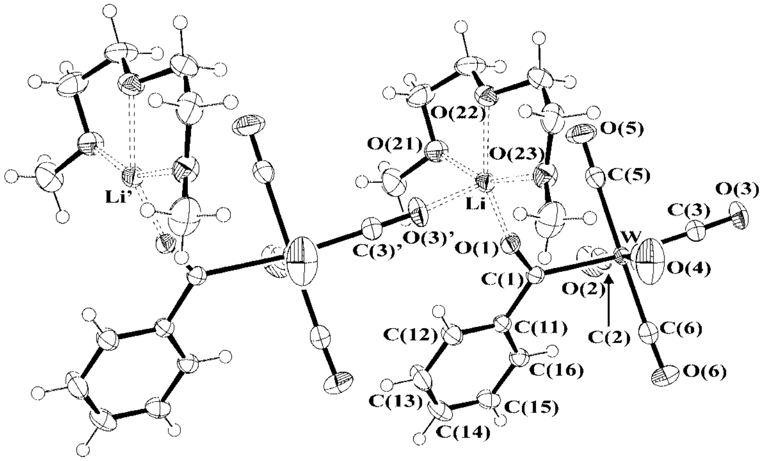


Figure 1. ORTEP[13] plot of **1** (two asymmetric units, 50% probability ellipsoids), showing the atomic numbering scheme and the polymeric structure observed in the crystal; selected bond lengths [Å] and angles [°]: W−C(1) 2.283(2), O(1)−C(1) 1.239(2), C(1)−C(11) 1.523(3), O(1)−Li 1.875(4), O(3)−Li 2.071(4), O(5)−Li 3.506(4), O(21)−Li 2.095(4), O(22)−Li 2.083(4), O(23)−Li 2.070(4), W−C(2) 2.026(2), W−C(3) 1.981(2), W−C(4) 2.047(2), W−C(5) 2.048(2), W−C(6) 2.024(3), C(2)−O(2) 1.150(3), C(3)−O(3) 1.164(3), C(4)−O(4) 1.136(3), C(5)−O(5) 1.137(3), C(6)−O(6) 1.143(3), C(1)−W−C(3) 171.8(1), C(2)−W−C(4) 175.0(1), C(5)−W−C(6) 179.5(1), W−C(1)−O(1) 119.9(2), W−C(1)−C(11) 126.6(1), O(1)−C(1)−C(11) 113.5(2), O(1)−Li−O(3)′ 105.2(2), O(1)−Li−O(21) 95.8(2), O(1)−Li−O(22) 150.5(2), O(1)−Li−O(23) 102.4(2), O(21)−Li−O(23) 154.1(2), O(3)′−Li−O(21) 95.6(2), O(3)′−Li−O(22) 104.1(2), O(3)′−Li−O(23) 97.3(2), W−C(2)−O(2) 178.8(2), W−C(3)−O(3) 178.3(2), W−C(4)−O(4) 178.0(3), W−C(5)−O(5) 179.2(2), W−C(6)−O(6) 177.5(2), O(1)−C(1)−C(11)−C(12) 8.9(3), C(5)−W−C(1)−O(1) 34.7(2)

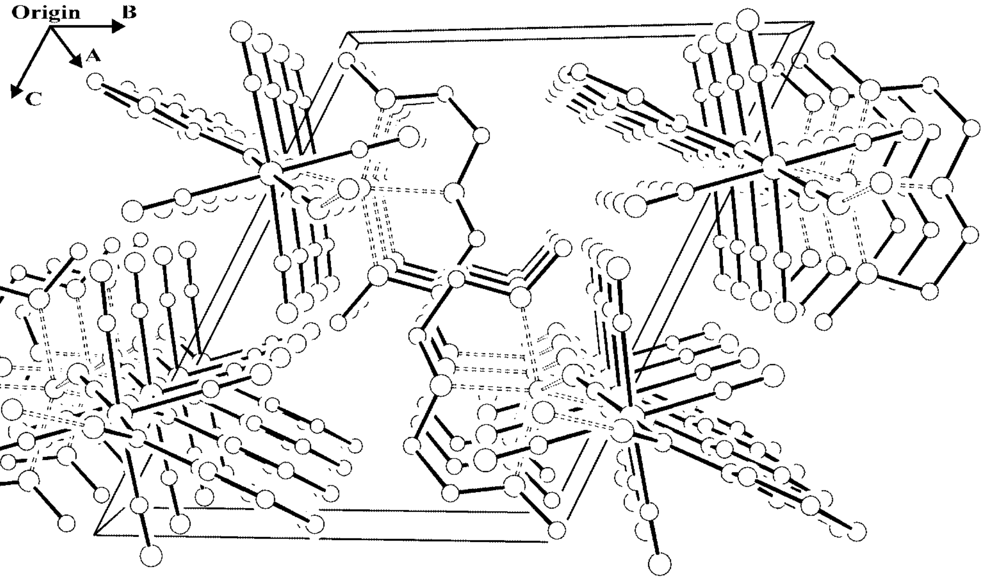


Figure 2. Packing diagram of **1**, viewed along the *a* axis, showing the extended structure of linked molecules (hydrogen atoms are omitted for clarity)

but sterically preventing the diglyme molecule from assuming a coordination mode that is closer to trigonal bipyramidal.

Interestingly the Li−O separations in the structure of **1** vary: Li to the diglyme oxygen atoms and to the CO ligand, O(3) are slightly shorter than in comparable five-coordinate Li[diglyme] structures [average of these four Li−O separations = 2.080(4) Å],[14] but the Li−acyl oxygen separation is still ca. 0.2 Å shorter than this [Li−O(1) = 1.875(4) Å]. In the absence of any obvious steric reasons, this difference within **1** indicates a much stronger electronic interaction between the Li$^+$ ion and O(1) than with other oxygen atoms.

The W−C(1) and C(1)−O(1) bond lengths [2.283(2) and 1.239(2) Å] in **1** are consistent with a small amount of charge delocalisation from the tungsten to the oxygen atom, due to Li$^+$-acyl coordination. Pure zero-valent tungsten W−C(sp^2) single bonds are usually slightly longer [≈ 2.31 Å][15] whereas uncoordinated acyl C=O double bonds are usually slightly shorter [≈ 1.21 Å].[16] An O(1)−C(1)−C(11)−C(12) torsion angle of 8.9(3)° describes the orientation of the phenyl ring toward the acyl moiety. The sp^2 hybridisation of C(1) is confirmed by its, within experimental error, flat bonding geometry [the greatest deviation from the least-squares plane through W, C(1), O(1), and C(11) is 0.004(2) Å for C(1)]. A C(5)−W−C(1)−O(1) torsion angle of 34.7(2)° describes how the benzoyl ligand is rotated relative to the $W(CO)_4$ coordination plane. Distortion of the $W(CO)_4$ coordination plane from planarity, due to bonding of the benzoyl ligand, is described by deviations from planarity from the least-squares plane through W, C(2), C(4), C(5) and C(6) of −0.0253(9), 0.0477(11), −0.0472(11), −0.0334(11), and −0.0362(12) Å respectively, and, furthermore, concurs with the relatively intense and infrared active B_1 absorption mode in the carbonyl region of the IR spectrum of **1** (see below).

In the crystal, asymmetric units of **1** pack in infinite polymeric chains, as described above, along the *a* axis of the unit cell in the triclinic centrosymmetric space group, $P\bar{1}$ (Figure 2). No significant intermolecular interactions, other than the intramolecular Li^+-bridges, are observed in the crystal structure of **1**. The highly ordered polymeric chain structure found for **1** might be partly responsible for the low crystal mosaicity [0.464(1)°] in the crystal selected for the X-ray diffraction study. It is noteworthy that this crystal yielded excellent diffraction data and that hence a very well-determined crystal structure was obtained for **1** [$R_1(I > 2\sigma I) = 1.38\%$].

Although lithium alkyl/aryl pentacarbonyl chromates/molybdates/tungstates are common organometallic intermediates in the synthesis of many alkyl/aryl alkoxy Fischer-type carbene complexes, the crystal structure of **1** appears to be the first example of this commonly employed organometallic Li^+-salt. The structure of a complicated lithium−(μ^2-benzoyl)-1,10-bis(diphenylphosphanyl)-(1,4,7,10-tetraoxadecane)$Mo(CO)_3$ complex, specifically designed to trap this Li^+ metallo−acyl species, has, however, been reported.[11a]

The crystal and molecular structure of **2** (Figure 3), although possessing a very similar empirical formula to **1** and containing the same metal carbonyl moieties, exhibits a completely different molecular arrangement. The structure of **2**, which is formally also a rare example of a hydrogen bond stabilised Fischer-type hydroxycarbene complex, clearly shows a Li^+ ion coordinated to two diglyme molecules, and two $Ph(O)CW(CO)_5^-$ ions linked via a strong, negative charge-assisted hydrogen bond between their acyl oxygen atoms. The striking difference in structure between **1** and **2** is down to the different interaction patterns of the cations. Protons, unlike Li^+ ions, are sufficiently stabilised in a two-coordinate hydrogen-bonded system while Li^+ ions can easily accommodate up to eight oxygen donor species and are rarely stabilised by less than four neutral oxygen donor atoms in the solid state.[17] Replacing half the Li^+ ions in solution thus allows the Li^+ ion to very efficiently coordinate to two diglyme molecules, whereas the strongly hydrogen-bonded proton in **2** is situated between two acyl groups of separate $Ph(O)CW(CO)_5^-$ ions.

The W−C(1) bond in **2** is slightly shorter than in **1** [W−C(1) = 2.238(5) Å in **2** vs. 2.284(2) Å in **1**] while the C(1)−O(1) bond in **2** is slightly longer [C(1)−O(1) = 1.276(6) Å in **2** vs. 1.239(2) Å in **1**]. These changes indicate a slight shift in electron density from the $W(CO)_5$ fragment

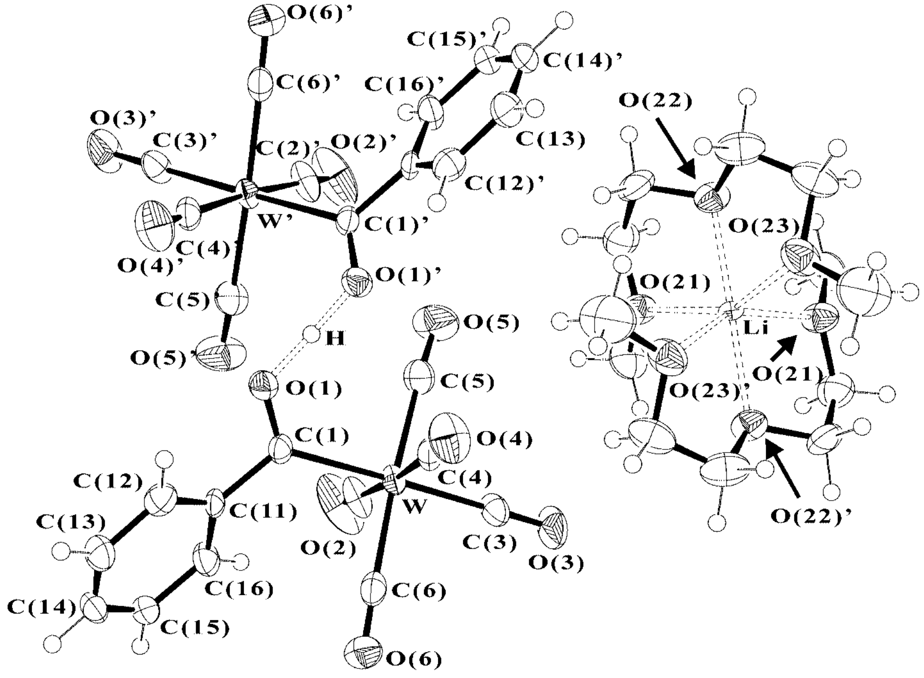


Figure 3. ORTEP[13] plot of **2** (two asymmetric units, 50% probability) showing the numbering scheme and charge-assisted hydrogen-bonding interactions observed in the crystal; selected bond lengths [Å] and angles[°]: W−C(1) 2.237(5), O(1)−H 1.233(12), O(1)−C(1) 1.277(6), C(1)−C(11) 1.505(7), O(1)−O(1)′ 2.442(6), W−C(2) 2.015(7), W−C(3) 1.996(6), W−C(4) 2.025(6), W−C(5) 2.044(6), W−C(6) 2.028(6), O(21)−Li 2.170(8), O(22)−Li 2.075(3), O(23)−Li 2.169(9), O(2)−C(2) 1.152(8), O(3)−C(3) 1.147(6), O(4)−C(4) 1.136(7), O(5)−C(5) 1.149(6), O(6)−C(6) 1.155(6), O(1)−H−O(1)′ 164.5(3), C(1)−W−C(3) 173.9(2), C(2)−W−C(4) 176.1(3), C(5)−W−C(6) 174.7(2), W−C(1)−O(1) 125.1(3), W−C(1)−C(11) 123.9(3), O(1)−C(1)−C(11) 110.7(4), W−C(2)−O(2) 176.4(5), W−C(3)−O(3) 178.5(6), W−C(4)−O(4) 178.5(5), W−C(5)−O(5) 175.2(5), W−C(6)−O(6) 177.4(5), O(21)−Li−O(23) 150.7(2), O(22)−Li−O(22)′ 167.8(6), C(5)−W−C(1)−O(1) 35.9(5), O(1)−C(1)−C(11)−C(12) 29.2(6)

to the acyl oxygen atom from **1** to **2** and suggest a stronger bonding interaction between the proton and the acyl oxygen atoms in **2** than between the Li^+ ion and the acyl oxygen atom in **1**. The O···O separation in **2** is very short [2.442(6) Å], showing that the hydrogen bond is indeed strong.[2] The position of the proton could be reliably determined and refined from the difference Fourier map and is, as expected in a hydrogen-bonding situation that involves identical anionic moieties, evenly spaced between the metallo-acyl oxygen atoms [O(1)−H = 1.232(11) Å].[18] The bridging hydrogen atom is, furthermore, situated on a crystallographic twofold rotation axis that lies parallel to the *c* axis of the unit cell and relates the anions in the formula unit to one another. Braga suggests that strong interanionic hydrogen bonds could be the result of a residual negative charge residing on the oxygen donor atoms.[2] In **2** this is clearly not the case. The bulk of the negative charge in anionic metallo-acyl metal carbonyl species is expected to be on the strongly electron-withdrawing $M(CO)_n$ fragments, as the W−C(1) and C(1)−O(1) bond orders and IR data, discussed below, of **1** and **2** reflect. Although some increase in the W−C(1) bond order and reduction of the C(1)−O(1) bond is seen upon hydrogen bonding in **2** (compared to **1**), the observed bond lengths and $\tilde{\nu}$(CO) absorption bands of **2** still suggest large amounts of negative charge delocalised onto the $W(CO)_5$ fragment. In $[(CO)_5W{=}C(OEt)Ph]$, in which some delocalisation of negative charge to the $W(CO)_5$ fragment is also present, these separations are 2.195 and 1.299 Å.[19] These observations suggest that the hydrogen bonding interactions observed in **2** are the result of classical hydrogen bonds and do not involve residual negative charge on the oxygen atom.[4d,20]

The Li^+ ion in **2** also resides on the twofold rotation axis in this space group, indicating that the $Li(diglyme)_2$ coordination possesses twofold symmetry. The crystallographic asymmetric unit of **2** thus consists of a single $Ph(O)CW(CO)_5^-$ ion hydrogen-bonded to a bridging proton, and one diglyme molecule coordinated to a shared Li^+ ion. Interestingly the hydrogen-bonded proton does not lie linearly between the metallo-acyl oxygen atoms [O(1)−H−O(1)′ = 164.5(3)°]; this measurement is not biased by the proton's crystallographically special position. The O(1)−H−O(1)′ angle depends on the unique coordinate of the proton along the *c* axis of the unit cell, which is free to change during the structure refinement. The reason for this kink in the hydrogen bond is not entirely clear. Similar kinks in hydrogen bonding interactions have, however, been reported between other anionic organometallic fragments and have been linked to weakening of the hydrogen bonding interaction, especially once the O−H−O angle exceeds 165°.[18,20]

An O(1)−C(1)−C(11)−C(12) torsion angle of 29.2(6)° describes the orientation of the phenyl ring toward the acyl moiety. Curiously, the sp^2 hybridisation of C(1) is somewhat more distorted from trigonal planar geometry than in **1**, possibly due to steric considerations [the respective deviations from the least-squares plane through W, C(1), O(1), and C(11) are 0.012(1), −0.044(4), 0.018(2), and 0.015(1) Å]. A C(5)−W−C(1)−O(1) torsion angle of 35.9(5)° is similar to that in **1**, and describes how the benzoyl ligand is rotated on the $W(CO)_4$ coordination plane. Distortion of the $W(CO)_4$ coordination plane from planarity, due to bonding of the benzoyl ligand, is also more than in **1**, and is described by deviations from planarity from the least-squares plane through W, C(2), C(4), C(5), and C(6) of −0.013(2), −0.057(3), −0.054(3), −0.063(3), and −0.061(3) Å, respectively. Coordination of the Li^+ ion to the six ether oxygen atoms of the two diglyme molecules in **2** is best described as a distorted, yet symmetrical, octa-

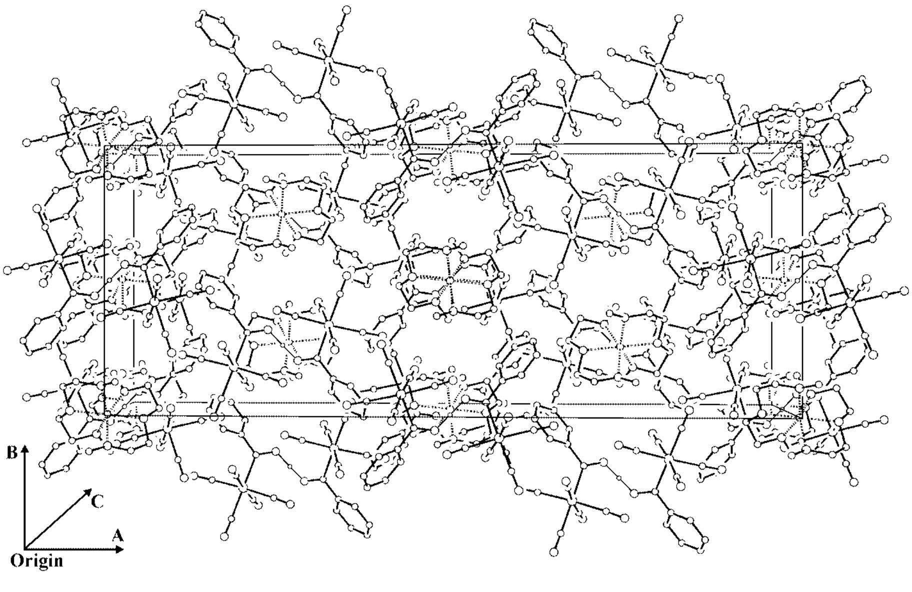


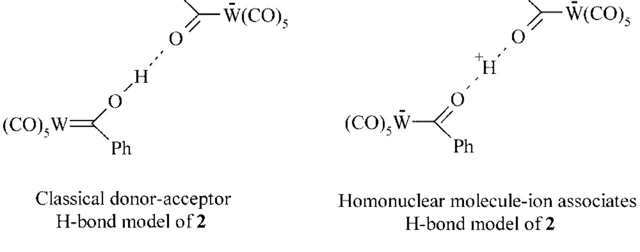
Figure 4. Packing diagram of **2**, viewed along the *c* axis of the unit cell, showing the packing arrangement of the dimeric H^+-bridged units in the crystal (all H atoms, except the bridging proton, have been omitted for clarity)

hedron with O(22) and its symmetry equivalent, O(22)′ occupying the axial positions. The Li−O separations in this arrangement are normal.[21]

In the crystal, **2** packs in the unusual orthorhombic and non-centrosymmetric face-centred space group, *Fdd*2. A view along the *c* axis of the unit cell (Figure 4) shows how eight hydrogen-bonded molecules (16 asymmetric units) pack in the unit cell with the bridging protons and Li^+ ions situated on the eight twofold rotation axes parallel to the *c* axis in this space group. No other significant intermolecular interactions were observed for **2**.

The crystal structures of hydroxycarbene complexes exhibit characteristic hydrogen bonding interactions involving the hydroxyl hydrogen atom. Of the 20 reported structures in the Cambridge Crystallographic Database[22] that can formally be regarded as hydroxycarbene complexes, 17 exhibit intramolecular hydrogen bonds [10c,23] while the remaining three exhibit intermolecular hydrogen bonds (two with $CF_3SO_3^-$ ions and one with an acetonitrile solvent molecule).[10a,10b,24] Consequently, the OH hydrogen atoms in hydroxycarbene complexes, without consideration of their spectroscopic or thermodynamic characteristics, are weakly linked to what is a pseudo metallo-acyl oxygen atom, and require further stabilisation through hydrogen bonding interactions. This interpretation is supported by the significant double bond character of the C(carb)−O bond in hydroxycarbene complexes (average C−O separation = 1.290 Å). The only neutron diffraction study of a hydroxycarbene complex, furthermore, reports a long O−H separation [1.142 Å].[10c] Hydroxycarbene complexes would therefore perhaps be better described as ion-paired [metallo−acyl][H] complexes, exhibiting hydrogen bonding interactions between acyl-oxygen atoms and a second donor atom, rather than complexes with a formal oxygen−hydrogen bond.

This approach enables a more accurate description of the hydrogen bonding interactions found in **2** as no classical donor−acceptor definitions are applicable. The hydrogen-bonded structure in **2** can thus be described as an anionic homonuclear molecule−ion associate of two $Ph(O)CW(CO)_5^-$ ions interacting with a proton, thus forming the strong, charge-assisted hydrogen-bonded complex found in the crystal (Scheme 2). Similar centred O···H···O hydrogen bonds have been described as quasi-covalent.[4d] Comparable μ_2-hydrogen-bonded structures have been reported for anionic organometallic cyanide complexes $[(CO)_5Cr\{C{\equiv}N\cdots H\cdots N{\equiv}C\}Cr(CO)_5]^-$ and $[(CO)_5Cr\{C{\equiv}N\cdots H\cdots N{\equiv}C\}FeCp(dppe)]$ [18] as well as for several carboxylate-functionalised sandwich compounds,[2,3] but not for complexes with metallo-acyl ligands.

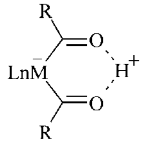


Classical donor-acceptor H-bond model of **2**

Homonuclear molecule-ion associates H-bond model of **2**

Scheme 2

Furthermore, of the 17 crystal structures of hydroxycarbene complexes that exhibit intramolecular hydrogen bonds, all but three [23j,23k,23l] contain two metallo-acyl moieties on a single metal atom involved in the hydrogen bonding interaction. This arrangement, forming six-membered metallacyclic rings (Scheme 3), is thus particularly favoured.



Scheme 3

The hydrogen bonding arrangement found in the crystal structure of **2** is similar to those described above (between two metallo-acyl groups), except that the metallo-acyl moieties involved in the hydrogen bonding interaction are on separate metal centres and, therefore, form a pseudo-linear hydrogen bonding arrangement. The structure of **2**, although novel, is thus not completely unexpected. Moreover, the structural characteristics of anionic metal−acyl complexes exhibited in the current structures, together with their general physical properties (e.g. stability, water solubility), firmly places them in the realm of suitable candidates for building blocks in organometallic crystal engineering. The selective introduction of a strong, charge-assisted hydrogen bonding interaction by selective Li^+ ion replacement in complex **2** may, furthermore, be a valuable tool to crystal engineers.

The infrared (IR) spectra of **1** and **2** were recorded as KBr pellets. The $\tilde{\nu}$(CO) absorption peaks for the CO ligands in both complexes exhibit the typical pattern of $A_1^{(1)}$, $A_1^{(2)}$, B_1, and E vibrational modes for molecules of the type $[M(CO)_5L]$ and are practically identical. The only clear deduction from the CO ligand stretching frequencies of **1** and **2** is that the metal atoms in these compounds are electron rich relative to other reported $[W(CO)_5L]$ complexes.[25] Comparison of the acyl C=O stretching frequencies [1517 cm^{-1} (**1**) and 1510 cm^{-1} (**2**)] is more fruitful. The 7 cm^{-1} lower C=O stretching frequency in **2** indicates that this bond is slightly more reduced in **2**, suggesting better interaction of the metallo-acyl anions with the proton in **2** than with the Li^+ ion in **1**, and corresponds to the results described by the crystal structures. The $\tilde{\nu}$(OH) frequency in **2** could, unfortunately, not be assigned reliably.

The IR spectrum of **1** was measured in CH_2Cl_2 solution. Dissolution of **1** causes a large change in the stretching frequency of the acyl vibrational mode (89 cm^{-1} "blue shift"). The $A_1^{(2)}$ vibration, assigned to the stretching frequency of the CO ligand trans to the metallo-acyl moiety, is unfortunately barely observable as a narrow shoulder on the intense E absorption peak in the solution IR spectrum of **1**, but is nevertheless shifted to higher energy (≈ 10−15 cm^{-1}).

These shifts strongly suggest that the clear interactions in the solid state of the Li^+ ions with the metallo acyl group, as well as with the CO ligand *trans* to the metallo acyl bond on a neighbouring anion, do not persist in dichloromethane solution. No interaction with Li^+ ions translates to less loss of electrons from the oxygen atoms in the groups that interact with the cation in the solid state and translates to stronger C≡O and C=O bonds in these groups.

The solution IR spectrum of **2** (CH_2Cl_2) is dominated by an extremely broad, intense and unresolved absorption band at ca. 1900 cm^{-1}. This is probably because, upon dissolution, **2** reverts, according to NMR spectroscopic data (discussed below), to a 50/50 mixture of Li[Ph(O)CW(CO)$_5$] and [Ph(OH)C=W(CO)$_5$] from whence it crystallised, and thus gives an IR spectrum for both compounds with broad, overlapping absorption bands. The ν(CO) for the acyl groups in this mixture as well as the ν(OH) absorption could, unfortunately, not be assigned reliably.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** are identical to the reported values,[12b] whereas the spectra of **2** contain partly overlapping resonances of both **1** and [Ph(OH)C=W(CO)$_5$]. For both compounds additional NMR resonances, representing 1 mol equiv. of diglyme, were also present. These resonances appear as a singlet at $\delta = 3.42$ (6 H, OCH$_3$) and two triplet signals at $\delta = 3.77$ and 3.66 ppm ($^3J_{H,H} \approx 5$ Hz, 4 H each), representing two sets of unique CH$_2$ groups in the diglyme molecule. In the $^{13}C\{^1H\}$ NMR spectra of **1** and **2** the resonances corresponding to diglyme appear at $\delta = 59.0$, 70.7, and 72.2.

Experimental Section

General: All reactions and manipulations were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. Et$_2$O was dried and purified by conventional methods and was freshly distilled under argon shortly before use. Melting points were measured with a Büchi 535 melting point determination apparatus and are uncorrected. NMR spectra were recorded on a Varian INOVA 600 spectrometer (^1H, 600 MHz; $^{13}C\{^1H\}$, 151 MHz; $^{31}P\{^1H\}$, 243 MHz) at 25 °C. NMR chemical shifts are reported in ppm relative to the ^1H and ^{13}C residue of the deuterated solvents. IR spectra were recorded on a Perkin−Elmer 1600 Series FTIR spectrometer. Elemental analyses were performed on a Fisons CHNS elemental analyser 1108. PhLi was prepared and standardised according to standard procedures. Diglyme and W(CO)$_6$ were purchased from Aldrich and used without purification.

Preparation of 1 and 2: PhLi (1.2 equiv., 0.6 mL, 1.6 M solution in Et$_2$O) was added dropwise to a suspension of W(CO)$_6$ (282 mg, 0.8 mmol) suspended in dry, degassed Et$_2$O (30 mL) over 30 min, and the resultant red reaction mixture was stirred for a further 1 h. Diglyme (1 equiv., 110 mg) was then added. To prepare crystals of **1** the volume of this mixture was reduced in vacuo to ca. 15 mL, carefully layered with an equal amount of *n*-pentane and cooled to −20 °C. $C_{18}H_{19}LiO_9W$ (570.13): calcd. C 37.9, H 3.36, O 25.3;

Table 1. Crystal data and structure refinement

Compound	1	2
Empirical formula	$C_{18}H_{19}O_9LiW$	$C_{36}H_{39}LiO_{18}W_2$
Formula mass [g/mol]	570.12	1134.29
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*F*dd2
a [Å]	8.8289(1)	37.8020(7)
b [Å]	11.1285(1)	14.8039(2)
c [Å]	12.9991(2)	15.1227(3)
α [°]	113.709(1)	90
β [°]	95.826(1)	90
γ [°]	108.179(1)	90
V [Å^3]	1072.55(2)	8462.9(3)
Z	2	8
$d_{calcd.}$ [g/cm^3]	1.765	1.781
T [K]	173(2)	173(2)
$\mu_{Mo\text{-}K\alpha}$ [cm^{-1}]	5.429	5.504
$2\theta_{max}$ [°]	26.00	26.00
Radiation	Mo-*K*α, graphite-monochromated	Mo-*K*α, graphite-monochromated
Crystal size [mm]	0.17 × 0.20 × 0.25	0.20 × 0.30 × 0.40
Index range	$-10 \le h \le 10$	$-46 \le h \le 36$
	$-13 \le k \le 13$	$-18 \le k \le 13$
	$-16 \le l \le 16$	$-17 \le l \le 18$
No. of reflections collected	8195	9371
No of independent reflections (R_{int})	4203 (0.0151)	3936 (0.0335)
Data/parameters	4203/264	3936/261
Refinement	Full matrix on F^2 (SHELXL)	Full matrix on F^2 (SHELXL)
Final *R* indices ($I > 2\sigma I$)	$R_1 = 0.0138$, $wR_2 = 0.0317$	$R_1 = 0.0249$, $wR_2 = 0.0487$
R indices (all data)	$R_1 = 0.0151$, $wR_2 = 0.0321$	$R_1 = 0.0304$, $wR_2 = 0.0501$
Largest diff peak and hole [e$^-$/Å^3]	0.476, −0.733	0.602, −0.907

found C 37.8, H 3.40, O 25.4. m.p. 76 °C. IR (KBr): ν(CO) = 2049 cm^{-1} (m, $A_1^{(1)}$), 1968 cm^{-1} (w, B_1), 1895 cm^{-1} (vs, E), 1885 cm^{-1} (m, sh, $A_1^{(2)}$), 1517 cm^{-1} (m, C=O). IR (CH_2Cl_2): ν(CO) = 2050 cm^{-1} (m, $A_1^{(1)}$), 1975 cm^{-1} (w, B_1), 1908 cm^{-1} (vs, E), ≈ 1895−1900 cm^{-1} (m, sh, $A_1^{(2)}$), 1606 cm^{-1} (m, C=O).

Crystals of **2** were prepared by filtering the red reaction mixture through acidic silica gel (10−15 cm, Ø 4 cm), using additional Et_2O to elute the red complex from the column. The volume of the elute was then reduced in vacuo to ≈ 15 mL, which was then carefully layered with an equal amount of *n*-pentane and cooled to −20 °C. $C_{36}H_{39}LiO_{18}W_2$ (1134.32): calcd. C 38.1, H 3.47, O 25.4; found C 38.0, H 3.40, O 25.5. m.p. 68 °C (decomp.). IR (KBr): ν(CO) 2049 cm^{-1} (m, $A_1^{(1)}$), 1968 cm^{-1} (w, B_1), 1904 cm^{-1} (vs, E), 1885 cm^{-1} (m, sh, $A_1^{(2)}$), 1510 cm^{-1} (m, C=O).

X-ray Crystallographic Analysis of 1 and 2: Suitable crystals of **1** and **2** were selected and mounted on glass fibres. Low temperature (173 K) diffraction data were collected for both crystals on a Nonius−Kappa CCD diffractometer,[26] equipped with an Oxford Cryostream cooling apparatus, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). A summary of the diffraction data is given in Table 1. Data sets for both crystals were scaled, reduced and corrected for Lorenz and polarisation effects using DENZO-SMN.[27] Both structures were solved by the interpretation of Patterson syntheses (SHELX-97),[28] which produced the positions of the metal atoms. The structures were completed by full-matrix least-squares calculations (SHELXL-97)[28] on F^2 and anisotropic thermal motion was allowed for all the non-hydrogen atoms during the final cycles of refinement. The space group in **2** is non-centrosymmetric; the Flack test[29] suggested the presence of a racemic twin and subsequent refinement revealed a racemic twin ratio of 0.886:0.114. Although the positions of most of the hydrogen atoms in **1** and **2** could be located from the difference Fourier map, all the hydrogen atoms situated on the phenyl rings were placed in idealised positions with their thermal parameters fixed at 1.2 times the equivalent isotropic displacement parameters of their parent atoms. The position of the bridging hydrogen atom in **2** could be reliably located from the difference Fourier map and refined isotropically. CCDC-211587 (**1**) and -211588 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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