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Reactions of 2-arsa- and 2-stiba-1,3-dionato lithium complexes with group 4–7 metal halides

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Abstract

The reactions of a range of 2-arsa- and 2-stiba-1,3-dionato lithium complexes with group 4–7 metals have been investigated. These have given rise to several complexes in which an arsadionate acts as a chelating ligand; $[V\{\eta^2\text{-O,O-OC(Bu}^t\text{)AsC(Bu}^t\text{)O}\}_3]$, $[M\{\eta^2\text{-O,O-OC(Bu}^t\text{)AsC(Bu}^t\text{)O}\}_2(DME)]$, M = Cr or Mn; or as an η^1-As-diacylarsenide, $[MnBr(CO)_4\{As[C(O)Bu^t]_2Li(DME)\}]_2$. In addition, reactions of lithium arsadionates with $TaCl_5$ have led to metal mediated arsadionate decomposition reactions and arsadionate oxidative coupling reactions to give the known arsaalkyne tetramer, $As_4C_4Bu^t_4$, and the new tetraacyldiarsane, $[\{As[C(O)Mes]_2\}_2]$ Mes = mesityl, respectively. The treatment of several lithium arsadionates with $[MoBr_2(CO)_2(PPh_3)_2]$ has also initiated arsadionate decomposition reactions and the formation of the metal carboxylate complexes, $[MoBr(CO)_2\{\eta^2\text{-}O_2C(R)\}(PPh_3)_2]$ R = Bu^t, Ph, Mes. The X-ray crystal structures of six of the prepared complexes are discussed.

Keywords: Arsenic; Antimony; Low coordination; Pnictadionates; Crystal structure

1. Introduction

The low coordination chemistry of phosphorus has become well established over the last 20 years. Studies in this area have revealed a close analogy between phosphorus and the valence isoelectronic CR fragment. In this respect phosphorus has been described as a ''carbon-copy'' [1]. In contrast, relatively little attention has been paid to the chemistry of low coordination arsenic and antimony compounds, probably due to the low thermal stability of these species, their toxicity and the absence of As or Sb isotopes with nuclear spin $I = 1/2$ [2]. Despite these problems, we have developed routes to several low coordination arsenic and antimony systems in recent years and have shown that their chemistry can be similar, but can also be significantly different to that of their phosphorus analogues.

One class of compound that we have been particularly interested in are the 2-pnicta-1,3-dionates, $[E\{C(O)R\}_2]^-$, **1** E = As or Sb, R = alkyl or aryl [3]. These are valence isoelectronic analogues of β-diketonates, the complexes of which are ubiquitous in inorganic chemistry [4] and have found numerous applications in areas ranging from catalysis to chemical vapour deposition (CVD) processes [5]. Considering the importance of β-diketonates as ligands, we have begun to explore the coordination chemistry of **1** with s-, p- and d-block metals. This is proving a fertile and versatile area of study. For example, whereas β-diketonates generally bind to main group and transition metals in variations of the chelating η^2-O,O-mode, the presence of 2-coordinate pnicogen centres in **1** has led to them exhibiting a variety of ligating modes which include η^2-O,O-; η^1-E; η^1-E:η^1-O:η^2-CO; η^1-E:η^2-O,O- and μ-η^1:η^1-E (as in, for example, **2**–**5**) [6]. In addition, the weakness of the E–C bonds in transition metal complexes of **1** can lead to their cleavage and the formation of novel and previously inaccessible complex types, for example the only known functionalised distibene which is stabilised in the complex, *cis*-$[Pt(PEt_3)_2\{\eta^2\text{-Sb,Sb-(Bu}^t\text{)(O)CSb=SbC(O)(Bu}^t\text{)}\}]$ [7].

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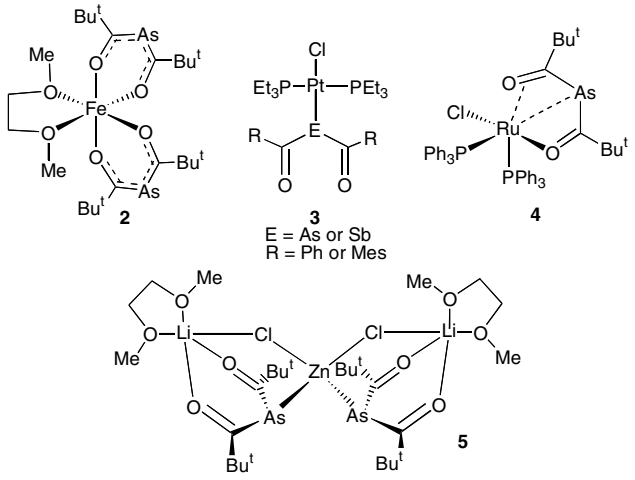
Despite the coordinative versatility of **1** towards transition metals, to date we have only reported on complexes of **1** with group 8–12 metals [6d], whilst complexes with group 4–7 metals remain unknown. In this paper we describe the preparation and characterisation of a series of such complexes, in addition to a number of unexpected results.



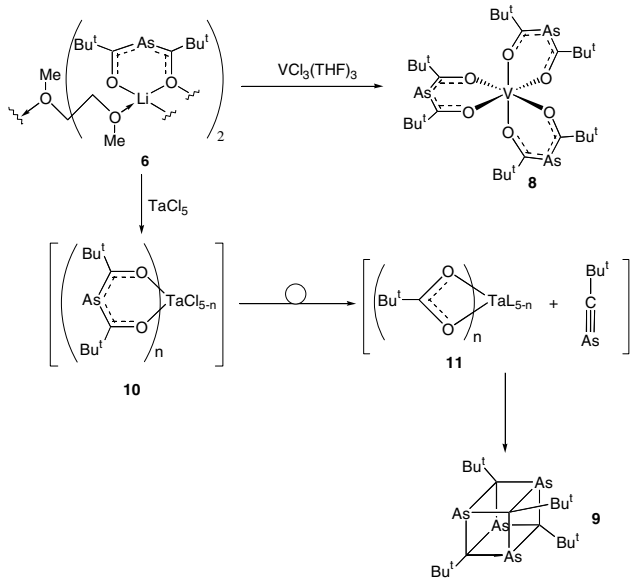
2. Results and discussion

2.1. Group 4

Numerous examples of group 4 β-diketonate complexes have been reported in the literature [4]. We have made many attempts to prepare pnictadionato analogues of these via the reactions of $[\{[Li\{\eta^2\text{-}O,O\text{-}OC(Bu^t)EC(Bu^t)O\}(DME)_{0.5}]_2\}_\infty]$, E = As **6**, Sb **7**, with MCl_4 and Cp_2MCl_2, M = Ti or Zr, using various stoichiometries of reagents. In all cases, however, rapid decomposition of the reaction mixtures at room temperature led to the deposition of either elemental arsenic or antimony and intractable mixtures of products. As a result, no further efforts were made in this area.

2.2. Group 5

The reaction of three equivalents of **6** with $[VCl_3(THF)_3]$ afforded a moderate yield of the first group 5 arsadionato complex, **8**, as large black crystals (Scheme 1). Interestingly, an attempt to prepare the related oxo-vanadium complex, $[V(=O)\{\eta^2\text{-}O,O\text{-}OC(Bu^t)AsC(Bu^t)O\}_2]$, via the 2:1 reaction of **6** with $VOCl_2$ in DME led to **8** in a low yield. When this reaction was repeated in a 4:1 stoichiometry, moderate yields (ca. 40%) of **8** resulted. The mechanism of this reaction is unclear but presumably involves the deoxygenation of the vanadium starting material by one



Scheme 1.

equivalent of the highly oxygen sensitive, **6**. It is worthy of mention that all attempts to prepare the antimony analogue of **8** by reaction of **7** with $[VCl_3(THF)_3]$ led to decomposition processes involving the deposition of antimony metal.

All attempts to obtain the X-ray crystal structure of **8** met with failure. It is likely, however, that it is an octahedral tris-chelate complex similar to related β-diketonate complexes, e.g., $[V(acac)_3]$, acac = acetylacetonoate [8]. Evidence for this proposal comes from its infrared spectrum which exhibits C–O stretching absorptions at 1502 and 1490 cm^{-1}, in the region consistent with delocalised, chelating arsadionate ligands [6e]. In contrast, it is known that when **1**, E = As, acts as a η^1-As-ligand it contains largely localised C–O double bonds which display stretching absorptions at significantly higher frequencies, ca. 1610–1680 cm^{-1} [6d,9]. This ligating mode is common in late transition metal complexes, e.g., **3**, but is unlikely for the oxophilic early transition metals. Compound **8** is paramagnetic with a μ_{eff} of 3.0 μ_B (Evans method [10]), as would be expected for a V^{3+} complex. As a result, no meaningful NMR data could be obtained on the compound.

An attempt to form a tantalum–arsadionate complex led to an unexpected result. The reaction of three equivalents of **6** with $TaCl_5$ in DME yielded the known tetraarsacubane, **9** [11], in a 14% yield (Scheme 1). The same product was obtained in lower yields when the reaction was carried out in 1:1, 2:1 or 4:1 stoichiometries. All attempts to elucidate the mechanism of this remarkable reaction failed but presumably it involves the initial formation of a chelated tantalum–arsadionate complex, **10**. This could then decompose via As–C and C–O bond cleavage reactions to give a transient arsaalkyne, $As{\equiv}CBu^t$, and tantalum carboxylate

complexes, e.g., **11**, or perhaps oxo-tantalum by-products. The generated arsaalkyne could then tetramerise to give **9**. Although this mechanism is speculative, especially as no tantalum carboxylate by-products were isolated from the reaction mixture, the products of reactions of **6** with group 6 halide complexes give it credence (vide infra). It is also interesting that the only previously reported preparation of the tetraarsacubane, **9**, involved the arsaalkyne, As≡CBu^t, as a transient intermediate in its formation [11]. In the present study **9** was characterised by its X-ray crystal structure which is isomorphous to that described in the prior report and therefore will not be commented on here. In addition, its ^{13}C NMR spectrum displays a characteristic high field shift (δ −46.5 ppm) for its framework carbon centres.

Arsaalkynes are very rare and indeed there is only one example that is stable at room temperature, As≡CMes*, Mes* = $C_6H_2Bu^t_3$-2,4,6 [12]. Unfortunately, the kinetic protection afforded by the bulky supermesityl substituent in this compound has limited the study of its further chemistry [13]. With this in mind, the formation of **9** raised the interesting possibility of preparing a variety of less hindered arsaalkynes (or arsaalkyne oligomers) using a similar synthetic procedure. To this end $TaCl_5$ or $NbCl_5$ were reacted with [Li{OC(R)As-C(R)O}(DME)], R = Ph **12** or mesityl (Mes) **13**, but in all cases the tetraacyl diarsanes, [{As[C(O)R]$_2$}$_2$] R = Ph **14**, Mes **15**, were formed in moderate yields, presumably via oxidative coupling of the arsadionate ligands by the M(V) precursors. It is not known why such couplings occur in these reactions when tetraarsacubane formation is seen in the reaction involving **6**, though perhaps the As–C bonds in the aryl substituted arsadionates are stronger and therefore less susceptible to cleavage.

Compound **14** has previously been reported by us [6d] but **15** is new. Its spectroscopic data are consistent with its proposed formulation which was confirmed by a single crystal X-ray structure determination (Fig. 1, Table 1). This shows the molecule to be dinuclear with two pyramidal arsenic centres generated by a crystallographic centre of inversion. The structure is very similar to that of **14** and the only other crystallographically authenticated tetraacyldiarsane, [{As[C(O)Bu^t]$_2$}$_2$] [14]. Both its As–C and As–As bond lengths are typical for single bonds and all the C–O distances are in the localised double bond range [15].

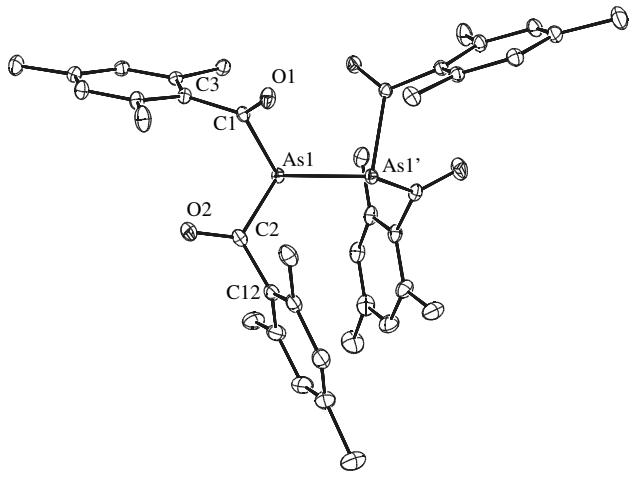


Fig. 1. Molecular structure of **15**. Selected bond lengths (Å) and angles (°): As(1)–C(2) 2.022(4), As(1)–C(1) 2.051(4), As(1)–As(1′) 2.4300(8), O(1)–C(1) 1.203(4), O(2)–C(2) 1.211(5), C(2)–As(1)–C(1) 89.62(15), C(2)–As(1)–As(1′) 98.13(11), C(1)–As(1)–As(1′) 94.86(10), O(1)–C(1)–As(1) 120.3(3), O(2)–C(2)–As(1) 117.5(3). Symmetry operation' $y, x, -z + 1/2$.

There have been no reported syntheses of stibaalkynes (Sb≡CR) or stibaalkyne oligomers. Given the preparation of **9**, it was thought that the reaction of the lithium stibadionate, **7**, with $TaCl_5$ might lead to

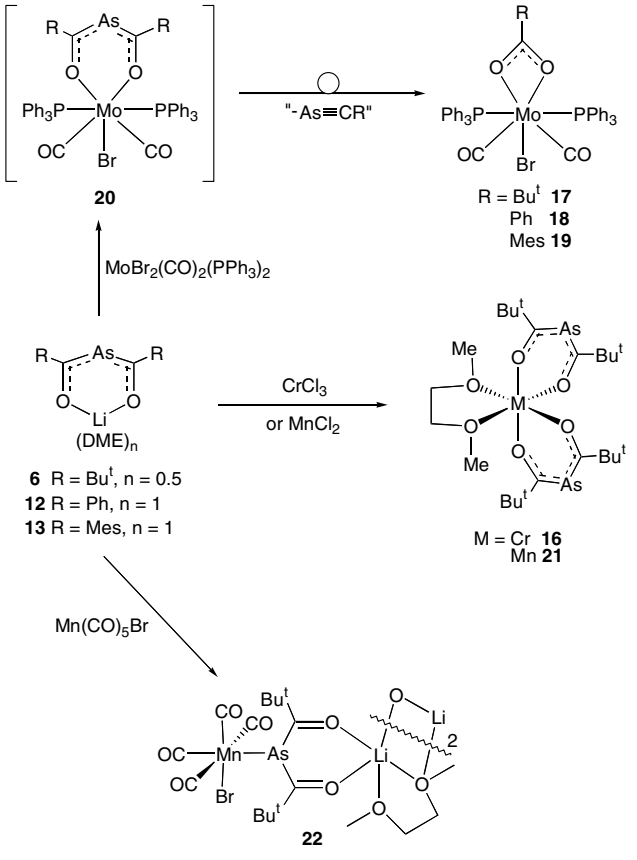
Table 1
Summary of crystallographic data for complexes **15**, **16**, **17** · Et_2O, **18** · Et_2O, **21** and **22**

	15	**16**	**17** · Et_2O	**18** · Et_2O	**21**	**22**
Chemical Formula	$C_{40}H_{44}As_2O_4$	$C_{24}H_{46}As_2CrO_6$	$C_{47}H_{49}BrMoO_5P_2$	$C_{49}H_{45}BrMoO_5P_2$	$C_{24}H_{46}As_2MnO_6$	$C_{36}H_{56}As_2Br_2Li_2Mn_2O_{16}$
Formula weight	738.59	632.45	931.65	951.64	635.39	1178.22
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{3}c_1$	$P_2(1)/n$	$P_2(1)/n$	$P_2(1)/n$	$C2/c$	$P_2(1)/n$
a (Å)	17.984(3)	10.986(2)	15.366(3)	13.164(3)	24.615(4)	10.548(2)
b (Å)	17.984(3)	15.334(5)	10.592(2)	17.657(4)	17.055(4)	17.295(4)
c (Å)	22.606(5)	18.633(6)	26.250(5)	19.377(4)	21.094(6)	13.578(3)
α (°)	90	90	90	90	90	90
β (°)	90	92.93(2)	94.61(3)	103.71(3)	128.20(2)	92.90(3)
γ (°)	120	90	90	90	90	90
V (Å^3)	6331.8(18)	3134.8(15)	4258.5(15)	4375.6(15)	6959(3)	2473.8(9)
Z	6	4	4	4	8	2
μ(Mo Kα) (mm^{-1})	1.616	2.491	1.367	1.332	2.295	3.513
Unique reflections	3734	5651	7761	7620	6252	5673
$R_1(I > 2\sigma(I))$	0.0572	0.0572	0.0583	0.1072	0.0470	0.0372
wR'_2(all data)	0.1080	0.1729	0.1334	0.3110	0.1350	0.0909

examples of these compounds. Unfortunately, however, the reaction only resulted in the deposition of elemental antimony and an oily intractable mixture of products. Analysis of this mixture by ^{13}C NMR did not reveal any high field (<−20 ppm) resonances that would be expected if a tetrastibacubane (cf. **9**) was present.

2.3. Group 6

Chromium tris(β-diketonate) complexes are ubiquitous in the literature [4]. In order to prepare an arsadionate analogue of this complex type, **6** was reacted in a 3:1 stoichiometry with $CrCl_3$ in DME. Surprisingly, this resulted in the moderate yield formation of the deep red Cr(II) complex, **16** (Scheme 2). The chromium reduction in this reaction is accompanied by the oxidative coupling of the arsadionate to form the known diarsane, $[\{As[C(O)Bu^t]_2\}_2]$, as a yellow crystalline solid. Solutions of **16** were shown to be paramagnetic with a μ_{eff} of 5.0 μ_B (Evans method [10]), corresponding to the metal centre having a high spin d^4 electronic configuration. The paramagnetic nature of the complex restricted the acquisition of meaningful NMR data but its infra-red spectrum displays a strong, broad absorption centred at 1501 cm^{-1}. This is consistent with the arsadionate ligands acting in a chelating mode, cf. the situation in **8**.



Scheme 2.

The X-ray crystal structure of **16** was obtained (Fig. 2, Table 1) and shows the complex to be monomeric with a distorted octahedral geometry, as is the case for the isomorphous Fe(II) complex, **2** [6d]. Another similarity with **2** is the fact that the arsadionate ligands are essentially planar and appear to be largely delocalised as all As–C bond lengths are similar (1.91 Å avg.) and lie between values normally seen for As–C single (1.96 Å) [16] and double bonds, e.g., 1.821(3) Å in $[CpFe(CO)_2As{=}CBu^t(OSiMe_3)]$ [17]. The Cr–O bonds associated with the arsadionate ligand (2.01 Å avg.) are significantly shorter than those arising from the DME ligand but similar to those in Cr(II)-β-diketonate complexes, e.g., 1.98 Å avg. in $[Cr(acac)_2]$ [18].

The reaction of the stibadionate, **7**, with $CrCl_3 \cdot DME$ did not lead to the antimony analogue of **16** but instead to an intractable mixture of products. Decomposition products also resulted from the reactions of **6** with $[MoBr_3(THF)_3]$, $[MoI_2(NCMe)_3]$, WCl_6 and $[CpMoCl_4]$ under a range of stoichiometries. In contrast, The 1:1 or 1:2 reactions of $[MoBr_2(CO)_2(PPh_3)_2]$ with a series of lithium arsadionates, **6**, **12** and **13**, led to very unusual outcomes, namely the moderate yield formations of the molybdenum carboxylate complexes, **17**–**19** (Scheme 2). In the 1:2 reactions the products, **17**–**19**, are apparently too hindered to allow reaction with the second equivalent of **6** which was recovered from the reaction mixture. The intermediates in these reactions are presumably the η^2-O,O-arsadionate complexes, **20**, which are unstable

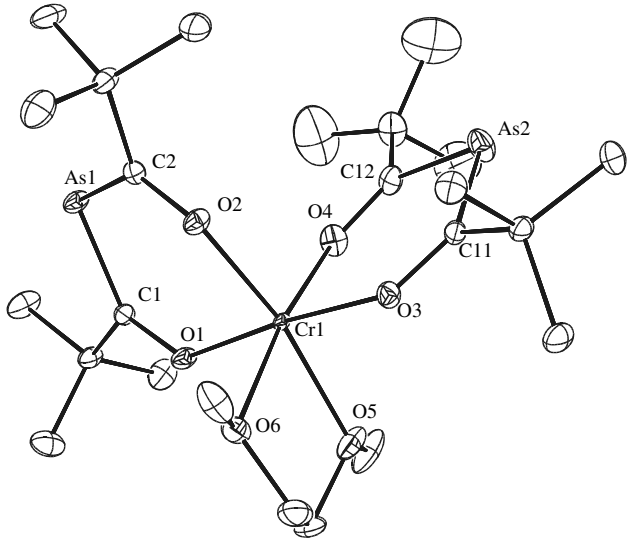


Fig. 2. Molecular structure of **16**. Selected bond lengths (Å) and angles (°): As(1)–C(1) 1.903(5), As(1)–C(2) 1.916(5), As(2)–C(11) 1.907(6), As(2)–C(12) 1.921(7), Cr(1)–O(3) 1.995(4), Cr(1)–O(4) 2.009(5), Cr(1)–O(2) 2.017(4), Cr(1)–O(1) 2.024(4), Cr(1)–O(5) 2.150(5), Cr(1)–O(6) 2.175(4), O(1)–C(1) 1.266(6), O(2)–C(2) 1.263(6), O(3)–C(11) 1.256(7), O(4)–C(12) 1.249(8), C(1)–As(1)–C(2) 101.8(2), C(11)–As(2)–C(12) 101.0(3), O(1)–Cr(1)–O(2) 90.8(2), O(3)–Cr(1)–O(4) 92.4(2), O(5)–Cr(1)–O(6) 76.8(2), As(1)–C(1)–O(1) 127.5(4), O(2)–C(2)–As(1) 126.6(4), O(3)–C(11)–As(2) 128.3(4), O(4)–C(12)–As(2) 127.9(5).

with respect to As–C and C–O bond cleavage and subsequent rearrangement to the observed carboxylate complexes. The by-products in these processes could be the arsaalkynes, As≡CR, R = Bu^t, Ph or Mes, or their oligomers, though these could not be isolated from the reaction mixtures or detected by ^{13}C NMR, TLC or GC/MS analyses. The parallels with the reaction between **6** and $TaCl_5$ are clear, and the formations of **17**–**19** add weight to the proposed formation of tantalum carboxylate by-products in that case.

All the spectroscopic data for **17**–**19** support their proposed structures and those for **18** are in close agreement with a previous report on this complex [19]. The crystal structures of **17** and **18** were obtained and are shown in Figs. 3 and 4 respectively (see Table 1). Both complexes are isostructural to each other and the closely related complex, $[MoBr(CO)_2\{\eta^2\text{-}O_2C(CF_3)\}(PPh_3)_2]$ [20]. As in this complex, the molybdenum centres in **17** and **18** can be described as 7-coordinate, having 4:3 geometries with the bromine and carboxylate oxygens occupying the triangular face, whilst the phosphine and carbonyl ligands form the quadrilateral face. The bond lengths and angles in both complexes are unexceptional and compare well to those in $[MoBr(CO)_2\{\eta^2\text{-}O_2C(CF_3)\}(PPh_3)_2]$.

2.4. Group 7

In the final stage of this study the reactivity of lithium arsa- and stibadionates towards manganese halide complexes was investigated. The reaction of two equivalents of **6** with $MnCl_2$ in DME afforded a moderate yield of the manganese-bis(arsadionate) complex, **21**, as an orange crystalline solid (Scheme 2). A magnetic susceptibility measurement (Evans method [10]) on this compound revealed a μ_{eff} of 5.3 μ_B which equates to a high spin d^5 complex, as would be expected. As in **8** and **16** its infrared spectrum exhibits C–O stretching absorptions in the normal range for chelating, delocalised arsadionate ligands. This was confirmed by a crystal structure determination (Fig. 5, Table 1) which shows the complex to be isostructural but not isomorphous with its chromium analogue, **16**, and thus to contain a distorted octahedrally coordinated metal centre. The average As–C and C–O bond lengths (1.91 and 1.25 Å respectively) are close to those in **16** and are suggestive of delocalised arsadionate ligands. Finally, the average Mn–O (arsadionate) distance (2.09 Å) compares well with the Mn–O separations in related manganese β-diketonate complexes, e.g., 2.03 Å avg. in $[Mn\{[OC(Bu^t)]_2CH\}_3]$ [21].

In previous studies [6d] we have shown that 2-pnicta-1,3-dionato ligands display a preference for η^1-E-coordination to the softer late transition metals, as in **3**, whereas in this study η^2-O,O-chelation to the harder early transition metals has proved to be the norm. As manganese is a mid transition metal, we predicted that it

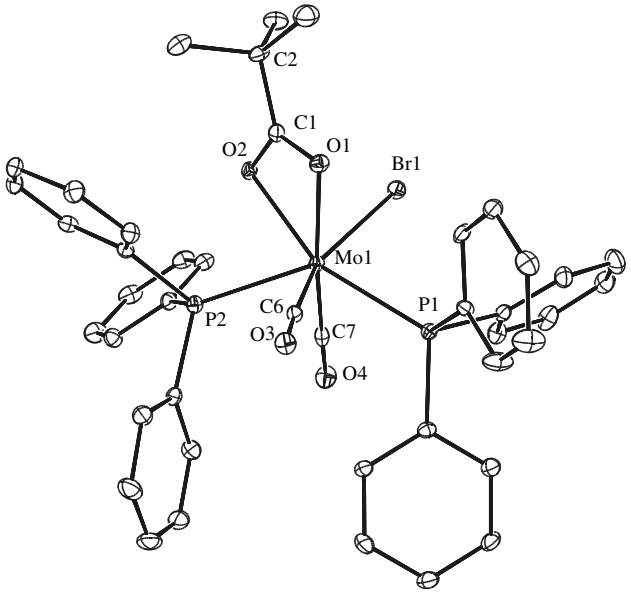


Fig. 3. Molecular structure of **17**. Selected bond lengths (Å) and angles (°): Mo(1)–O(2) 2.231(4), Mo(1)–O(1) 2.246(4), Mo(1)–P(2) 2.4591(16), Mo(1)–P(1) 2.5297(15), Mo(1)–Br(1) 2.6069(9), C(1)–O(1) 1.262(6), O(2)–C(1) 1.279(6), O(1)–C(1)–O(2) 117.9(5), O(2)–Mo(1)–O(1) 58.17(13), P(1)–Mo(1)–P(2) 130.37(5), C(7)–Mo(1)–C(6) 105.4(2).

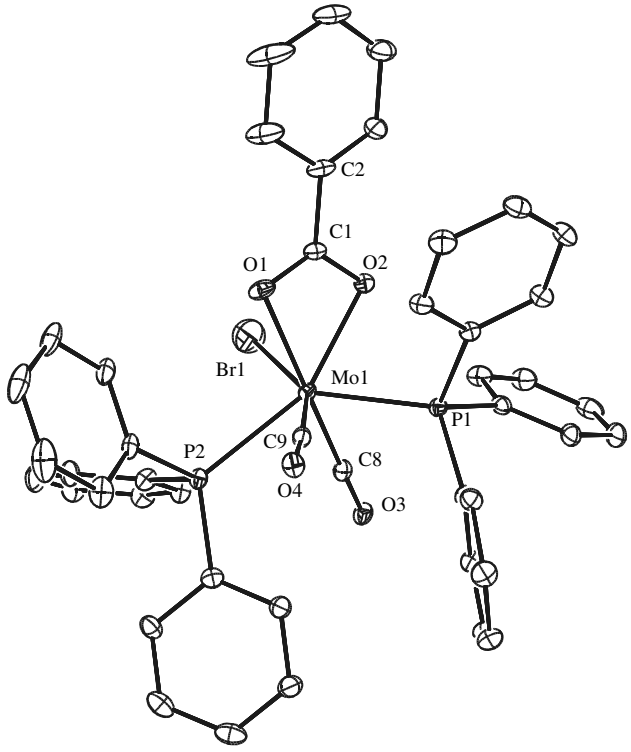


Fig. 4. Molecular structure of **18**. Selected bond lengths (Å) and angles (°): Mo(1)–O(2) 2.232(6), Mo(1)–O(1) 2.233(6), Mo(1)–P(2) 2.519(2), Mo(1)–P(1) 2.482(2), Mo(1)–Br(1) 2.500(2), C(1)–O(1) 1.262(11), O(2)–C(1) 1.281(10), O(1)–C(1)–O(2) 119.1(7), O(2)–Mo(1)–O(1) 58.8(2), P(1)–Mo(1)–P(2) 131.23(7), C(8)–Mo(1)–C(9) 104.6(3).

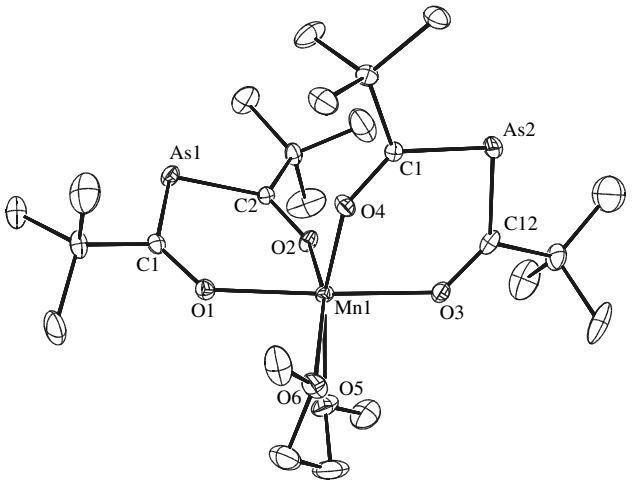


Fig. 5. Molecular structure of **21**. Selected bond lengths (Å) and angles (°): As(1)–C(1) 1.917(5), As(1)–C(2) 1.906(4), As(2)–C(11) 1.914(4), As(2)–C(12) 1.925(5), Mn(1)–O(3) 2.100(3), Mn(1)–O(4) 2.088(3), Mn(1)–O(2) 2.091(3), Mn(1)–O(1) 2.109(3), Mn(1)–O(5) 2.232(4), Mn(1)–O(6) 2.279(4), O(1)–C(1) 1.261(5), O(2)–C(2) 1.255(5), O(3)–C(12) 1.248(6), O(4)–C(11) 1.238(5), C(1)–As(1)–C(2) 101.33(19), C(11)–As(2)–C(12) 100.0(2), O(1)–Mn(1)–O(2) 85.32(12), O(3)–Mn(1)–O(4) 85.38(12), O(5)–Mn(1)–O(6) 71.99(16), As(1)–C(1)–O(1) 126.9(3), O(2)–C(2)–As(1) 126.6(3), O(3)–C(12)–As(2) 127.3(3), O(4)–C(11)–As(2) 127.8(3).

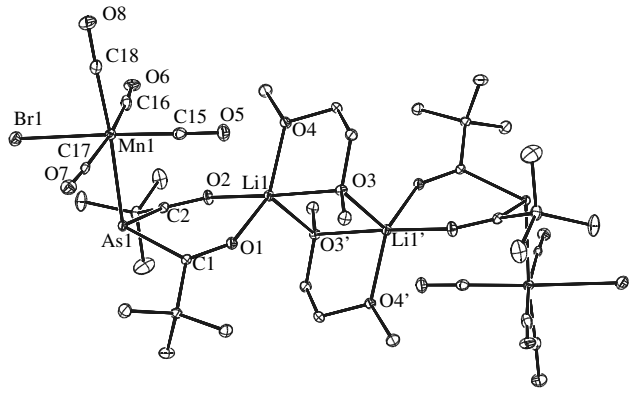


Fig. 6. Molecular structure of **22**. Selected bond lengths (Å) and angles (°): As(1)–C(2) 2.017(3), As(1)–C(1) 2.026(3), As(1)–Mn(1) 2.5596(7), Mn(1)–Br(1) 2.5163(7), O(3)–Li(1) 2.197(6), O(3)–Li(1′) 2.142(6), O(1)–C(1) 1.225(4), O(1)–Li(1) 1.963(6), O(2)–C(2) 1.215(4), O(2)–Li(1) 1.988(6), O(4)–Li(1) 1.976(6), C(1)–As(1)–C(2) 92.77(12), C(2)–As(1)–Mn(1) 102.00(9), C(1)–As(1)–Mn(1) 105.92(8). Symmetry operation' $-x, -y, -z$.

may show intermediate properties. It seemed possible that although η^2-O,O-chelation was observed for the Mn(II) complex, **21**, η^1-As-ligation might predominate in Mn(I) systems. To test this hypothesis **6** was reacted with $[Mn(CO)_5Br]$ in a 1:1 stoichiometry. This reaction led to an unexpected outcome, namely the moderate yield formation of the dimeric complex, **22**, after recrystallisation from hexane (Scheme 2). In this reaction CO displacement from the manganese precursor has occurred instead of the intended salt elimination reaction which would give $[Mn(CO)_5\{\eta^1\text{-}As[C(O)Bu^t]_2\}]$, **23**. As compound **22** could be considered as an intermediate in the expected salt elimination reaction, it was slowly heated as a DME solution to 80 °C under an atmosphere of CO. This did not, however, lead to **23** but instead to decomposition and the formation of an intractable mixture of products. Likewise, the reaction of **7** with $[Mn(CO)_5Br]$ led to the deposition of elemental antimony and no other reaction products could be identified.

Complex **22** can be regarded as an anionic diacylarsenido-manganese(I) complex which is coordinated to its lithium counter-ion. It is of note that we have previously observed a range of related complexes which are putative salt elimination reaction intermediates, e.g., $[(COD)Rh\{As[C(O)Ar]_2[LiCl(OEt_2)]\}]$ $Ar = C_6H_2Pr^i_3$-2,4,6; $[Zn\{As[C(O)Bu^t]_2[LiCl(DME)]\}_2]$ and $[LiCl(Et_2O)(DME)\{\eta^2\text{-}O,O\text{-}Cl_3InAs[C(O)R]_2\}]$ [6]. The spectroscopic data for **22** support its proposed formulation. Specifically, its infra-red spectrum exhibits a strong acyl CO stretching absorption at 1644 cm^{-1} which is in the region normally observed for localised diacylarsenido ligands. Moreover, there are four strong overlapping bands between 1926 and 2057 cm^{-1}, as might be expected for a *cis*-substituted octahedral metal carbonyl complex.

The structure of **22** was confirmed by an X-ray crystal structure analysis (Fig. 6, Table 1) which shows the molecule to be dimeric through bridging DME molecules, giving rise to a planar Li_2O_2 ring. The coordination environment about the manganese centre is distorted octahedral with the Br and As centres in *cis*-positions. Interestingly, the As–Mn separations [2.5596(7) Å] are easily the longest yet reported for 3-coordinate arsenic centres (the mean As–Mn distance of structurally characterised compounds is 2.413 Å) [15]. This anomaly likely arises due to the steric bulk of the diacylarsenido ligands. The Mn–Br bonds [2.5163(7) Å] are in the normal region for such interactions. In contrast to near planar, delocalised arsadionate ligands in complexes such as **16** and **21**, the diacylarsenide ligands in **22** are not planar and contain pyramidal arsenic centres (Σ angles = 300.7°), each presumably having a stereochemically active lone pair. In addition, both the As–C (2.03 Å avg.) and C–O distances (1.22 Å avg.) are indicative of localised single and double bonds respectively. The oxygen centres of these ligand chelate the 5-coordinate lithium counter-ions of the complex.

3. Conclusion

In summary, we have described the reactions of a range of 2-arsa- and 2-stiba-1,3-dionato lithium complexes with group 4–7 metal halide complexes. Although little success was had with the formation of stibadionato

complexes, as series of η^2-O,O-arsadionato metal complexes have been prepared and structurally characterised. In addition, in one complex, **22**, the pnictadionate acts as an η^1-As:η^2-O,O-bridging diacylarsenido ligand. A remarkable tantalum mediated decomposition of an arsadionate ligand has also been reported to give rise to the known arsaalkyne tetramer, $As_4C_4Bu^t_4$. The mechanism of this reaction has been suggested to involve an intermediate tantalum–arsadionate complex which decomposes to give $As_4C_4Bu^t_4$ and an unidentified tantalum carboxylate by-product. The formation of molybdenum carboxylate complexes in related reactions adds some weight to this proposal. The results of the work described herein have been compared with those of our earlier studies on pnictadionato late transition and main group metal complexes and highlight the coordinative versatility of this ligand class.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. DME and hexane were distilled over potassium whilst diethyl ether was distilled over Na/K alloy. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DXP400 spectrometer operating at 400.13 and 100.6 MHz respectively and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. ^{31}P{^{1}H} NMR spectra were recorded on a Jeol Eclipse 300 spectrometer and were referenced to external 85% H_3PO_4, 0.0 ppm. Mass spectra were recorded using a VG Fisons Platform II instrument operating under APCI conditions. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Magnetic susceptibilities were determined using the Evans method, corrected for super-conducting NMR instruments [10]. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were carried out by the Warwick Analytical Service. The 2-arsa- and 2-stiba-1,3-dionatolithium starting materials, **6**, **7**, **12** and **13**, were prepared by variations of literature methods [3,6]. $[MoBr_2(CO)_2(PPh_3)_2]$ was prepared by a literature procedure [22]. All other reagents were obtained commercially and used as received.

4.1. $[V\{\eta^2\text{-}O,O\text{-}OC(Bu^t)AsC(Bu^t)O\}_3]$ **8**

A solution of **6** (0.443 g, 1.49 mmol) in DME (40 ml) was added dropwise to a solution of $[VCl_3(THF)_3]$ (0.186 g, 0.50 mmol) in DME (30 ml) at −78 °C. The resulting dark red solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark brown residue which was extracted with hexane (3×30 ml), filtered and the filtrate concentrated to ca. 10 ml. This was placed at −30 °C overnight yielding **8** as black crystals (yield: 0.16 g, 41%), m.p. >200 °C; $\mu_{eff} = 3.0\ \mu_B$; IR (Nujol, ν/cm^{-1}) AsCO 1502 s, 1490 s; MS APCI: m/z 787 (MH^+, 100%); calc. for $C_{30}H_{54}O_6As_3V$: C 45.76, H 6.93. Found: C 45.70, H 6.86%.

4.2. $As_4C_4Bu^t_4$ **9**

A solution of **6** (0.15 g, 0.51 mmol) in DME (40 ml) was added dropwise to a solution of $TaCl_5$ (0.06 g, 0.17 mmol) in DME (30 ml) at −78 °C. The resulting yellow solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark yellow residue which was extracted with hexane (3×30 ml), filtered and the filtrate concentrated to ca. 15 ml. This was placed at −30 °C overnight yielding **9** as yellow crystals (yield: 0.01 g, 14%). Spectroscopic data and melting point as reported [11].

4.3. $[\{As[C(O)Mes]_2\}_2]$ **15**

A solution of **13** (0.854 g, 2.03 mmol) in DME (50 ml) was added dropwise to a solution of $TaCl_5$ (0.240 g, 0.68 mmol) in DME (40 ml) at −78 °C. The resulting dark red solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark brown residue which was washed with hexane (10 ml), extracted with DME (20 ml), filtered and the filtrate concentrated to ca. 10 ml. This was placed at −30 °C overnight yielding **15** as colourless needles (yield: 0.28 g, 38%), m.p. 153–154 °C (dec.); NMR: ^{1}H (400 MHz, C_6D_6), δ 2.11 (s, 12H, p-ArCH$_3$), 2.52 (s, 24H, o-ArCH$_3$), 6.76 (s, 8H, ArH); ^{13}C (100.6 MHz, C_6D_6), δ 19.1, 19.6 (ArCH$_3$), 128.1 (m-Aryl C), 132.8 (o-Aryl C), 138.2 (p-Aryl C), 140.2 (*ipso*-Aryl C), 219.1 (As–C); IR (Nujol, ν/cm^{-1}) AsCO 1667 s, 1641 s; MS APCI: m/z: 369 (M^+/2, 100%).

4.4. $[Cr\{\eta^2\text{-}O,O\text{-}OC(Bu^t)AsC(Bu^t)O\}_2(DME)]$ **16**

A solution of **6** (0.36 g, 1.21 mmol) in DME (40 ml) was added dropwise to a suspension of $CrCl_3$ (0.064 g, 0.40 mmol) in DME (30 ml) at −78 °C. The resulting purple suspension was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark red residue which was extracted with hexane (3×30 ml), filtered and the filtrate concentrated to ca. 20 ml. This was placed at −30 °C overnight yielding **16** as red crystals (yield: 0.114 g, 41%), m.p. 112–113 °C (decomp); $\mu_{eff} = 5.0\ \mu_B$; IR (Nujol, ν/cm^{-1}) AsCO 1501 br; MS APCI: m/z (%): 58 (HBu^{t+}, 100), 543 (M^+−DME, 15), 245 ($AsO_2C_2Bu^t_{2+}$, 13); calc. for $C_{24}H_{46}As_2CrO_6$: C 45.57, H 7.20. Found: C 45.81, H 6.97%.

4.5. $[MoBr(CO)_2\{\eta^2\text{-}O_2C(Bu^t)\}(PPh_3)_2]$ 17

A solution of **6** (0.203 g, 0.69 mmol) in DME (50 ml) was added dropwise to a suspension of $[MoBr_2(CO)_2(PPh_3)_2]$ (0.286 g, 0.34 mmol) in DME (50 ml) at −78 °C. The resulting blue suspension was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark brown residue which was extracted with diethyl ether (3 × 30 ml), filtered and the filtrate concentrated to ca. 10 ml. This was placed at −30 °C overnight yielding **17** as red crystals (yield: 0.13 g, 41%), m.p. 127–129 °C (dec.); NMR: ^{1}H (400 MHz, C_6D_6), δ 0.92 (9H, s, Bu^t), 6.91 (m, 12H, *m*-ArH), 7.13 (m, 12H, *o*-ArH), 7.72 (m, 6H, *p*-ArH); ^{13}C (100.6 MHz, C_6D_6), δ 27.3 [C(*C*H$_3$)], 66.3 [*C*(CH$_3$)], 131.0 (*m*-aryl C), 133.5 (*o*-aryl C), 134.0 (*p*-aryl C), 135.1 (*ipso*-aryl C), 197.5 (CO_2); ^{31}P{^{1}H} (121.7 MHz, C_6D_6) δ 64.3 (s); IR (Nujol, ν/cm^{-1}) CO 1941(m), 1854 (s), CO_2 1580 (m); MS: APCI *m*/*z* (%): 263 ($HPPh_3^+$, 100).

4.6. $[MoBr(CO)_2\{\eta^2\text{-}O_2C(Ph)\}(PPh_3)_2]$ 18 and $[MoBr(CO)_2\{\eta^2\text{-}O_2C(Mes)\}(PPh_3)_2]$ 19

Complexes **18** (yield: 25%) and **19** (yield: 20%) were prepared by a similar procedure used for the preparation of **17**. The spectroscopic data for **18** are identical to those reported [19]. The data for **19** are as follows; m.p. 132–133 °C (dec.); NMR: ^{1}H (400 MHz, C_6D_6), δ 2.01 (s, 3H, *p*-ArCH$_3$), 2.53 (s, 6H, *o*-ArCH$_3$), 6.75 (s, 2H, Mes-ArH), 7.2–8.0 (m, 30H, ArH); ^{13}C (100.6 MHz, C_6D_6), δ 19.6, 21.4 (ArCH$_3$), 127.0, 127.1, 127.4, 128.8, 129.3, 133.4, 138.7, 139.1 (ArC), 185.0 (CO_2); ^{31}P{^{1}H } (121.7 MHz, C_6D_6) δ 64.6 (s); IR (Nujol, ν/cm^{-1}) CO 1954 (m), 1866 (s), CO_2 1603 (m); MS: APCI *m*/*z* (%): 263 ($HPPh_3^+$, 100).

4.7. $[Mn\{\eta^2\text{-}O,O\text{-}OC(Bu^t)AsC(Bu^t)O\}_2(DME)]$ 21

A solution of **6** (0.327 g, 1.10 mmol) in DME (40 ml) was added dropwise to a solution of $MnCl_2$ (0.069 g, 0.55 mmol) in DME (30 ml) at −78 °C. The resulting yellow/orange solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving an orange/brown residue which was extracted with hexane (3 × 30 ml), filtered and the filtrate concentrated to ca. 10 ml. This was placed at −30 °C overnight yielding **21** as orange crystals (yield: 0.123 g, 35%), mp 110–111 °C (dec.); $\mu_{eff} = 5.3\ \mu_B$; IR (Nujol, ν/cm^{-1}) AsCO 1562 s, 1592 s; MS APCI: *m*/*z* (%): 635.9 (M^+, 100); calc. for $C_{24}H_{46}As_2MnO_6$: C 45.35, H 7.24%. Found: C 45.73, H 7.42%.

4.8. $[MnBr(CO)_4\{As[C(O)Bu^t]_2Li(DME)\}]_2$ 22

A solution of **6** (0.267 g, 0.90 mmol) in DME (40 ml) was added dropwise to a solution of $[Mn(CO)_5Br]$ (0.247 g, 0.90 mmol) in DME (40 ml) at −78 °C. The resulting red solution was allowed to warm to room temperature and stirred for 24 h. Volatiles were removed in vacuo leaving a dark orange/red residue which was extracted with hexane (3 × 30 m1), filtered and the filtrate concentrated to ca. 25 ml. This was placed at −30 °C overnight yielding **22** as orange/red crystals (yield: 0.15 g, 29%), m.p. 59–60 °C (dec.); NMR: ^{1}H (400 MHz, C_6D_6), δ 1.30 (36H, s, Bu^t), 3.10 (s, 12H, OMe), 3.31 (s, 8H, OCH_2); ^{13}C (100.6 MHz, C_6D_6), δ 25.2 (C(*C*H$_3$)$_3$), 50.5 (*C* Me3), 57.9 (OMe), 68.9 (OCH_2), 215.9 (MnCO), 253.1 (AsC); IR (Nujol, ν/cm^{-1}) AsCO 1645 s, 1598 s; MnCO 2057, 1982, 1961, 1926; MS APCI *m*/*z* (%): 245 (As{C(O)Bu^t}$_2^+$, 100), 679 ($MnBr(CO)_4\{As[C(O)Bu^t]_2Li(DME)_2\}^+$, 23); calc. for $C_{36}H_{56}As_2Br_2Li_2Mn_2O_{16}$: C 36.67, H 4.75. Found: C 35.46, H 4.63%.

4.9. Crystallographic studies

Crystals of **15**, **16**, **17**, **18**, **21** and **22** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either Nonius CAD-4 or Kappa-CCD diffractometers. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX 97) [23] using all unique data. The data for **18** were poor, leading to a high *r*-factor, but the molecular connectivity of this complex is unambiguous. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **15**, **16**, **17**, **18**, **21** and **22** have been deposited with the Cambridge Crystallographic Data Centre **15**: CCDC no. 230102; **16**: CCDC no. 230103; **17** CCDC no. 230104; **18**: CCDC no. 230105; **21**: CCDC no. 230106; **22**: CCDC no. 230107. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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