

Cite this: *Dalton Trans.*, 2024, **53**, 11959Electrophilic As-functionalisation of σ -arsolido complexes†

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The σ -arsolido complex $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ is alkylated at arsenic by MeOTf to afford the pentamethylarsole complex $[\text{Mo}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)](\text{OTf})$ while iodomethane affords a mixture of $[\text{Me}_2\text{AsC}_4\text{Me}_4]$, $[\text{MoMe}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$, $[\text{MoI}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ and the arsole complexes *cisoid*- and *transoid*- $[\text{MoI}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ and *transoid*- $[\text{Mo}(\text{C}(\text{=O})\text{Me})(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$. The arsole ligand in $[\text{Mo}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)](\text{OTf})$ is readily liberated by NaI in acetone to afford free $\text{MeAsC}_4\text{Me}_4$ and $[\text{MoI}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$. In a similar manner, the reaction of $[\text{Mo}(\text{AsC}_4\text{Ph}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ with MeI affords $\text{MeAsC}_4\text{Ph}_4$ and $[\text{MoI}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$, while $[\text{Mo}(\text{AsC}_4(\text{SiMe}_3)_2\text{-Me}_2\text{-3,4})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ with MeOTf affords $[\text{Mo}(\text{MeAsC}_4(\text{SiMe}_3)_2\text{-Me}_2\text{-3,4})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)](\text{OTf})$. The reaction of $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ with activated alkynes ($\text{RC}\equiv\text{CR}$; $\text{R} = \text{CF}_3, \text{CO}_2\text{Me}$) does not proceed *via* [4 + 2] *cyclo*-addition but rather electrophilic attack at arsenic followed by metallacyclisation with incorporation of a carbonyl ligand in the spirocyclic complexes $[\text{Mo}(\text{As}(\text{C}_4\text{Me}_4)\text{CR}=\text{CRCO})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$.

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Introduction

Although a small number of σ -arsolyl (arsolido) complexes have been reported,¹ little is known concerning their reactivity, beyond a proclivity towards self-condensation to afford homobimetallic μ -arsolido complexes (a) or the addition of extraneous metal centres to generate heterobimetallic μ -arsolido complexes.² They appear to be plausible intermediates in the ultimate formation of *pentahapto*-arsolyl complexes,^{1b,3} and in one case redox disproportionation of the chromium σ -arsolyl $[\text{Cr}(\text{AsC}_4\text{Ph}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ affords convenient access to a diarsolyl $(\text{AsC}_4\text{Ph}_4)_2$.^{2c} It stands to reason that by analogy with the demonstrated arsenic-centred nucleophilicity of σ -arsenido complexes $\text{L}_n\text{M-AsR}_2$,⁴⁻⁶ σ -arsolyls should display similar arsenic-centred nucleophilicity. This would be supported by the recent computational interrogation of the complexes $[\text{Mo}(\text{AsMe}_2)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ *vs.* $[\text{Mo}(\text{AsC}_4\text{H}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ that showed that the 'lone' pair on arsenic is most certainly available for electrophilic attack, rather than being otherwise involved in establishing a Hückel sextet for the *pseudo*-aromatic arsole ring (Fig. 1).^{3c}

This has however yet to be experimentally explored beyond the simple addition of coordinatively unsaturated metal

centres, *e.g.*, 'AuC₆F₅', 'Mn(CO)₂($\eta^5\text{-C}_5\text{H}_4\text{Me}$)' and 'Fe(CO)₂($\eta^5\text{-C}_5\text{H}_5$)⁺' to $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (**1a**).² Accordingly, we now report an investigation of the reactivity of a series of σ -arsolyl complexes of molybdenum, *viz.* $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (**1a**), $[\text{Mo}(\text{AsC}_4\text{Ph}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (**1b**) and $[\text{Mo}(\text{AsC}_4\text{H}(\text{SiMe}_3)_2\text{-Me}_2\text{-3,4})(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (**1c**) towards electrophilic alkylating agents and *potentially* dienophilic electrophilic alkynes.

Results and discussion

The σ -arsolyl complexes **1a-1c** are now readily available *via* facile transmetalation between the stannyl complex $[\text{Mo}(\text{Sn}^n\text{Bu}_3)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ and the corresponding As-chloro-arsoles ClAsC_4R_4 ($\text{R} = \text{Me}, \text{Ph}$) or $\text{ClAsC}_4(\text{SiMe}_3)_2\text{-2,5-Me}_2\text{-3,4}$, the latter being accompanied by an unusual monodesilylation of one arsole ring substituent (Scheme 1).^{1c}

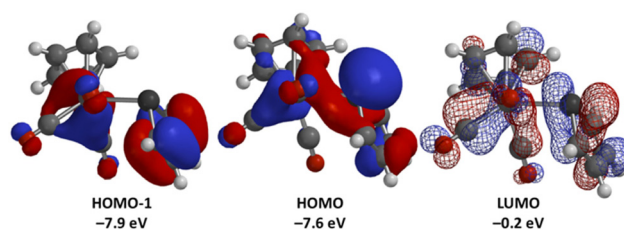
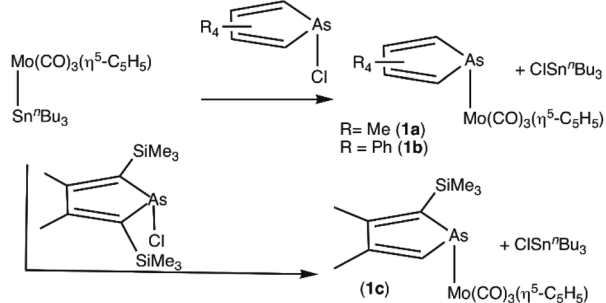


Fig. 1 Valence orbitals of interest for the complex $[\text{Mo}(\text{AsC}_4\text{H}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$.^{3c}

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Scheme 1 Synthesis of σ -arsolyl complexes via transmetalation.^{2c}

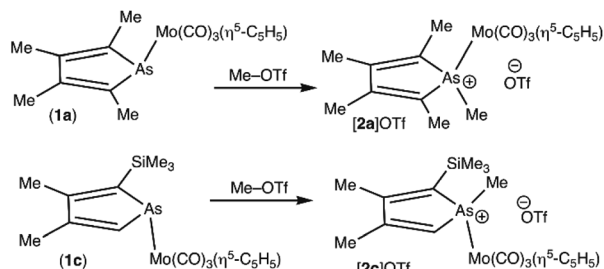
The complex **1a** is readily alkylated at the heteroatom by methyl trifluoromethanesulfonate (MeOTf, OTf = SO₃CF₃) in Et₂O solution at 0 °C. Bright yellow, X-ray quality crystals of the salt [Mo(MeAsC₄Me₄)(CO)₃(η^5 -C₅H₅)]OTf [**2a**]OTf rapidly precipitated from solution and the product was isolated in near-quantitative yield (86%, Scheme 2). Care must be taken to avoid too great an excess of MeOTf which results in decomposition to oily black residues.

Spectroscopic data reflect the formal localisation of positive charge at the molybdenum centre with a shift of ν_{CO} absorptions to higher wavenumbers (CH₂Cl₂: 2057(vs), 1998(sh), 1965(vs) cm⁻¹), and a shift of the ¹H cyclopentadienyl resonance from 5.16 ppm (CD₂Cl₂) in **2a** to higher frequency (5.54 ppm) in the cationic [**2a**]⁺. The As-CH₃ group resonance in the ¹H NMR spectrum (CD₂Cl₂: δ_H = 1.66) is to slightly lower frequency of the ring methyl groups (δ_H = 1.95, 1.82) which are essentially identical in chemical shift to those of the precursor **1a**, being seemingly unaffected by alkylation of the arsenic. A shift to higher frequency is observed in the ¹³C{¹H} NMR spectrum for the carbonyl ligands *transoid* (225.8 ppm) and *cisoid* (223.2 ppm) to the pentamethylarsole ligand (*cf.* 235.5 and 224.7 ppm for **1a** in CD₂Cl₂) as the efficacy of Mo(*d*) \rightarrow CO(π^*) back-bonding is reduced; the same argument applies to the cyclopentadienyl signal (93.5 *vs.* 94.3 ppm). The arsolyl ring-carbon nuclei are similarly displaced to slightly higher frequency by As-methylation (145.8 and 134.5 ppm *vs.* 149.1 and 141.8 ppm for **1a**), a feature which also manifests in binuclear complexes of the μ -AsC₄Me₄ ligand^{2b} as the modest ring-current within the cyclic system is further diminished by appropriation of the arsenic lone pair. High-resolution mass

spectrometry (ESI) reveals extensive fragmentation of the molecular ion, the primary mode of disintegration being loss of the arsenic-bound CH₃ group in addition to sequential products of decarbonylation; single crystals suitable for X-ray diffraction were collected from the reaction mixture and the molecular structure is shown in Fig. 2.

Crystallographic inspection of the reaction product confirms As-methylation. Reflecting the formal positive charge on the Mo(II) atom and the change in bonding description (X to L⁷) between the metal and pnictogen, a contraction of the Mo-As distance by almost 0.15 Å to 2.5844(4) Å is noted (*cf.* 2.7267(7) Å for **1a**). A similar contraction (though of lesser magnitude) is observed upon coordination of Lewis acidic metal centres to **1a**.^{2b} Apparently, sequestration of the arsenic lone pair alleviates a repulsive interaction with the electronically saturated molybdenum centre, permitting closer approach of the two centres – the so-called transition metal *gauche* effect described by Gladysz.⁸ The arsenic atom adopts a deformed tetrahedral geometry with external bonding angles of 105–117° and an internal C-As-C ring-angle of *ca.* 89°. The pentamethylarsole ligand is swivelled about the Mo-As bond to lie in an unsymmetrical disposition about the molecule, similar to that found in **1b**,²² at the expense of the intramolecular C-H... π contact found in the solid state structure of **1a**. Interatomic distances within the arsole ring are reflective of decreased aromatic character with a slight compression of the C _{α} =C _{β} bonds (mean 1.327(5) Å) and elongation of the C _{β} -C _{β} bond (1.496(5) Å) compared to the neutral arsolyl complex (1.351(7) and 1.469(8) Å, respectively), though these variations lie at the precision limits of the data.

Alkylation of **1c** was explored similarly: treatment with MeOTf in Et₂O solution causes the product [**2c**]OTf to rapidly precipitate from solution in excellent yield (81%) as bright yellow crystals suitable for X-ray diffraction. Spectroscopic features are comparable to those of the pentamethylarsole complex [**2a**]⁺ and accordingly, only salient features are noted. The solution IR spectrum reveals the usual trio of carbonyl vibrations (CH₂Cl₂: 2065(vs), 1992(sh), 1971(vs) cm⁻¹) shifted to higher wavenumbers from **1c** (2007(vs), 1938(sh), 1922(vs) cm⁻¹), and the resonance for the olefinic hydrogen α to the



Scheme 2 Monomethylation of σ -arsolyl complexes.

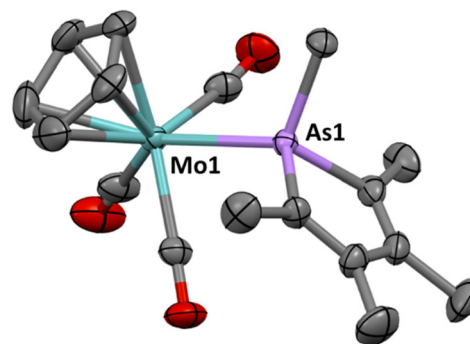


Fig. 2 The molecular structure of [**2a**]⁺ in a crystal of [**2a**]OTf (50% displacement ellipsoids, hydrogen atoms and triflate anion omitted).

arsenic atom appears at 6.97 ppm in CD_2Cl_2 solution. The cyclopentadienyl ligand resonances appear at 5.82 and 92.4 ppm in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively, and the carbonyl ligands at 235.7 (*transoid*), 225.6 and 223.6 ppm (diastereotopic *cisoid*) in the latter. The four chemically inequivalent arsole ring-carbon nuclei are found at 158.4, 157.1, 149.7 and 146.7 ppm with the resonance at $\delta_{\text{C}} = 149.7$ corresponding to the methylidyne carbon as indicated by both HSQC NMR measurements, and by nOe enhancement. The molecular structure was determined by X-ray diffractometry and is shown in Fig. 3.

The molecular structure of $[\mathbf{2c}]^+$ in $[\mathbf{2c}]\text{OTf}$ is largely similar to that of $[\mathbf{2a}]^+$. The arsole ligand lies “sideways” against the $\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ centre with the SiMe_3 group occupying the region of space between the *cisoid* carbonyl ligands. The As→Mo dative bond length of 2.6016(6) Å is slightly longer than that in $[\mathbf{2a}]^+$ (2.5844(4) Å), though it is noted that the Mo–As covalent bond in $\mathbf{1c}$ is also *ca.* 0.02 Å longer than in $[\mathbf{2a}]^+$ no doubt due to the intrinsic proximal steric influence of the SiMe_3 residue. Dimensions of the arsole ring follow the same pattern as for $[\mathbf{2a}]^+$ with a compression of the inequivalent $\text{C}_\alpha=\text{C}_\beta$ bonds (1.326(6), 1.342(6) Å) and elongation of the $\text{C}_\beta-\text{C}_\beta$ bond (1.489(6) Å) upon methylation of the arsenic atom, compared to neutral $\mathbf{1c}$.

The tetraphenylarsolyl complex $\mathbf{1b}$ undergoes alkylation with reluctance. Treatment with MeOTf in toluene solution gives no immediate precipitation of a salt, and only upon standing for several days at ambient temperature do a very small quantity of yellow crystals form which were regrettably unsuitable for X-ray diffractometry; accompanying these crystals were a larger quantity of oily brown residues. Dissolution of the isolated crystals precipitated more of these insipid residues and $\text{MeAsC}_4\text{Ph}_4$ ($\mathbf{3}$, Fig. 5) was the only identifiable species. The same outcome was obtained in CH_2Cl_2 solution which resulted in $\mathbf{3}$ being the only isolable product. The observation that tetraphenylarsoles are generally hesitant to quarterisation suggests a very poorly nucleophilic arsenic centre, in line with observations to follow involving methyl iodide as the alkylating agent. Geometrical minimisation at the $\omega\text{B97X-D}/6\text{-31G}^*/\text{LANL2DZ}$ level of density functional theory^{2c} returns rather similar natural charges (+0.678 a.u. for $\mathbf{1a}$; +0.677 a.u. for $\mathbf{1b}$) and negligible atom-condensed Fukui functions ($f^+ =$

0.005 for $\mathbf{1a}$; 0.002 for $\mathbf{1b}$). The latter are somewhat misleading because for $\mathbf{1a}$ the arsenic lone pair lies only 0.1 eV below the HOMO which is associated with the butadiene component of the arsolyl group. For $\mathbf{1b}$, the energy gap is larger (0.4 eV) and the HOMO is delocalised out to the 2,5-phenyl substituents. This suggests that the low nucleophilicity of $\mathbf{1b}$ is primarily due to the steric bulk surrounding the arsenic (Fig. 4) rather than any significant electronic impact. The tetraphenylarsolyl complex $\mathbf{1b}$ is, however, cleaved by an excess of CH_3I in solution overnight to provide $[\text{MoI}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (^1H NMR (C_6D_6): δ 4.44 ppm. IR (CH_2Cl_2): 2043(vs), 1961(vs) cm^{-1}) and 1-methyl-2,3,4,5-tetraphenylarsole ($\mathbf{3}$) as the only products by NMR spectroscopy. Repeating the reaction in CH_2Cl_2 on a preparative scale allowed isolation of the dark red molybdenum iodide complex (83%) and the light yellow $\text{MeAsC}_4\text{Ph}_4$ arsole ($\mathbf{3}$, 70%, Fig. 5) in high yields.

The reaction almost certainly proceeds *via* initial methylation of the arsenic atom (which may or may not follow a radical pathway, *vide infra*) followed by rapid and irreversible nucleophilic substitution of the arsole ligand from the $[\text{Mo}(\text{MeAsC}_4\text{Ph}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]^+$ $[\mathbf{2b}]^+$ complex by the iodide anion. This process is presumably dissociative in nature since the Mo(II) centre is both electronically-saturated and seven-coordinate, and the displacement of the arsole ligand from the cationic complex must be at least as rapid as its formation since at no point during the reaction were any other cyclopentadienyl signals observed in the ^1H NMR spectrum (Scheme 3).

The more nucleophilic $\mathbf{1a}$ also reacts with excess CH_3I in C_6D_6 solution, though the reaction was considerably more complex than anticipated (Scheme 4). Multiple products are generated, including large colourless crystals of $[\text{Me}_2\text{AsC}_4\text{Me}_4]\text{I}$

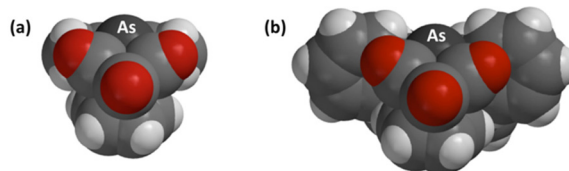


Fig. 4 Corey–Pauling–Kolton models for (a) $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ and (b) $[\text{Mo}(\text{AsC}_4\text{Ph}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$.

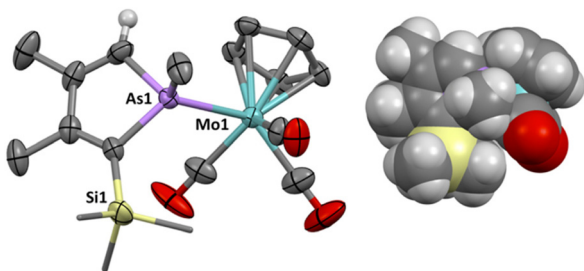


Fig. 3 The molecular structure of $[\mathbf{2c}]^+$ in a crystal of $[\mathbf{2c}]\text{OTf}$ (50% displacement ellipsoids, Si-methyls simplified and most hydrogen atoms and triflate anion omitted). Inset: Space-filling representation.

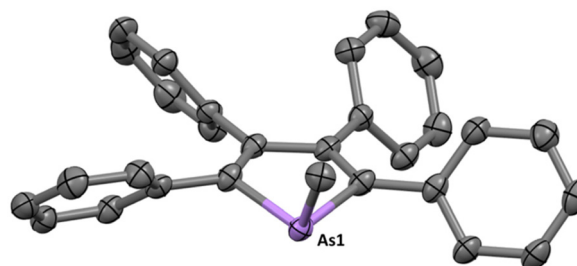
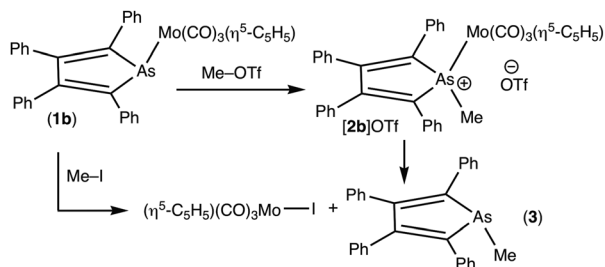
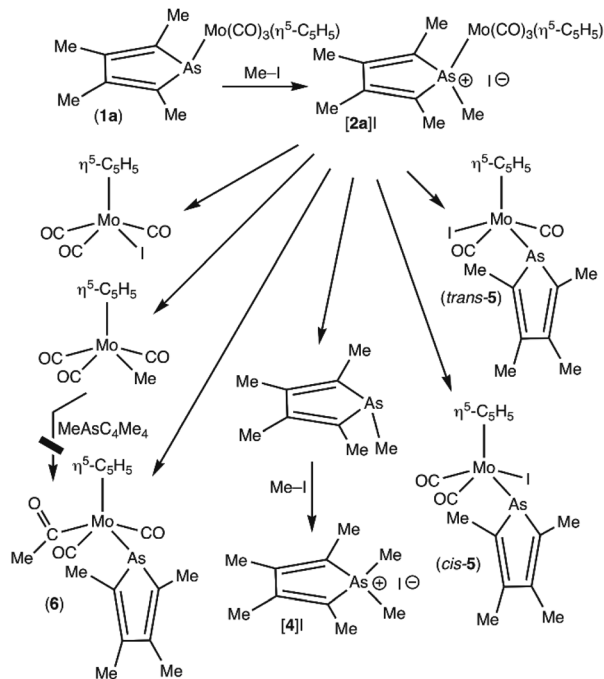


Fig. 5 The molecular structure of $\text{MeAsC}_4\text{Ph}_4$ ($\mathbf{3}$) in a crystal (50% displacement ellipsoids, phenyl groups simplified and hydrogen atoms omitted for clarity). The As–Me moiety is disordered over two positions and only the major contributor is shown.



Scheme 3 Attempted methylation of a tetraphenylarsolyl complex.



Scheme 4 The reaction of **1a** with excess iodomethane.

[**4**]I which separate in 62% yield from solution. This salt is the first example of an authentic cationic arsole (henceforth arsolium), although there are examples of annulated arsoles undergoing quaternisation.⁹ These are excluded from the present discussion given the ring system is not based on a localised butadiene moiety, one of the major identifying features of arsoles. The salt [**4**]I was structurally characterised and the molecular geometry of the cation is shown in Fig. 6 in addition to the unit cell packing which indicates weak hydrogen bonding (≈ 3.0 Å) between the iodide and protons on four methyl groups.

The arsolium salt [**4**]I was isolated from the reaction mixture in good yield and was fully characterised. The internal symmetry of the cation is reflected in the ^1H NMR spectrum (CDCl_3) which finds only three equally integrating signals at 2.58, 2.32 and 2.00 ppm of which the latter is assigned to the arsenic-bound methyl groups by comparison with the As-methyl resonance in [**2a**]OTf. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

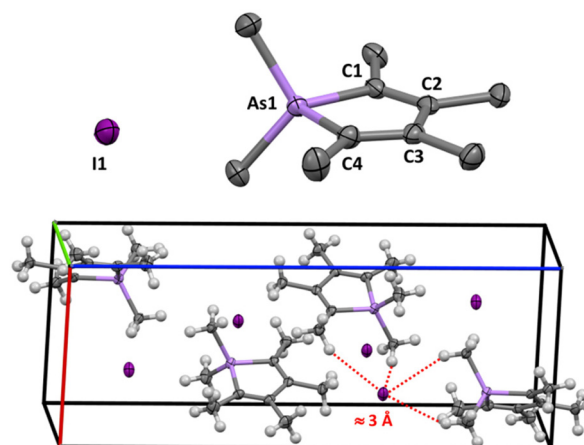


Fig. 6 The molecular structure of [**4**]I in a crystal (50% displacement ellipsoids, methyl groups simplified and hydrogen atoms omitted). Inset: The unit cell contents ($P2_1/c$) viewed along the crystallographic b axis highlighting extended $\text{H}\cdots\text{I}^-$ interactions.

the arsolyl ring-carbon nuclei manifest at 150.3 and 123.5 ppm (α and β to the heteroatom, respectively) with three methyl environments at 15.0, 14.2 and 9.2 ppm. The latter is identified as the arsenic-bound methyl carbon atoms on the basis of HSQC and HMBC NMR experiments. High-resolution mass spectrometry reveals the molecular ion in high intensity ($m/z \approx 213.0628$). The formation of [**4**]I was confirmed in a separate experiment to arise from simple alkylation of $\text{MeAsC}_4\text{Me}_4$ by methyl iodide. Methyl triflate will also alkylate pentamethylarsole in Et_2O at 0°C , though the [**4**]OTf salt formed degraded over several weeks in the solid state (under argon) to oily brown residues. Conversely, the iodide salt retained its integrity for >2 years. Other methylating agents such as $[\text{Me}_3\text{O}]\text{BF}_4$ were not tested. Methyltetraphenylarsole $\text{MeAsC}_4\text{Ph}_4$ (**3**) did not undergo such a reaction, recalling the resistance of **1b** to alkylation. A reasonable course of events involves initial alkylation of the arsenic in $[\text{Mo}(\text{AsC}_4\text{Me}_4)(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ to form a salt [**2a**]I, from which dissociation of the arsole is followed by irreversible coordination of the iodide counter anion.

Hexamethylarsolium iodide [**4**]I crystallises (monoclinic $P2_1/c$) with four separated cation–anion pairs contained in the unit cell. Incidentally, the iodide anions have distorted bisphe-noidal coordination geometry ($\tau_4 = 0.86$, $\tau'_4 = 0.57$) in the solid-state since only four hydrogen bonds operate (per iodide) with approximate valence angles of *ca.* 165° (*pseudo-trans* axial) and 82° (*pseudo-equatorial*). The [**4**]⁺ cation is approximately though not crystallographically laterally-symmetric (C_{2v}), and the quaternary arsenic atom exists in a distorted tetrahedral environment with external (local) bonding angles of 109 – 118° , though the internal $\text{C}_\alpha\text{-As-C}_\alpha$ vertex is regular within this work at 88° . Compared to other RAsC_4Me_4 arsoles which have been structurally characterised,¹⁰ interatomic distances within the $[\text{Me}_2\text{AsC}_4\text{Me}_4]^+$ cation reflect a true 2,4-diene localisation of the π -electron density about the ring with a contraction of the As-C_α (mean $1.903(3)$ Å) and $\text{C}_\alpha=\text{C}_\beta$ bonds (mean $1.327(4)$ Å),

and an elongation of the $C_{\beta}-C_{\beta'}$ bond (1.500(3) Å). That said, exploration of the molecular orbital manifold for the model cation $[\text{Me}_2\text{AsC}_4\text{H}_4]^+$ (DFT: ω B97X-D/6-31G*, Fig. 7) does suggest a modest contribution from arsenic to the π -system (HOMO-1, HOMO-4). It is also noteworthy that rather than the arsenic, as is typical for conventional arsonium cations, C_{α} and $C_{\alpha'}$ would be expected to be the preferred sites for frontier orbital-controlled nucleophilic attack considering the topologies of the LUMO, as well as the atom-condensed Fukui functions (f^-)¹¹ for arsenic ($f^- = 0.024$) and C_{α}/α' ($f^- = 0.184$). This is despite the arsenic carrying a substantial natural positive charge (+1.63 a.u.). Such processes would be expected to yield dimethyl(butadienyl)arsines ($\text{Me}_2\text{AsCH}=\text{CHCH}=\text{CH}-\text{Nu}$), however this propensity would be somewhat curtailed in the real cases of arsolylums bearing C_{α} -substituents, as most do.

As an aside, the colourless arsolylum [4]I did appear to react with $\text{Li}^{\text{n}}\text{Pr}_2$ in Et_2O solution at -78 °C to provide a cherry-red solution, presumed to contain an arsenic ylide $\text{H}_2\text{CAsMeC}_4\text{Me}_4$ (by analogy with H_2CAsPh_3 ¹²) which, however, decomposed to poorly-soluble light brown materials upon warming. The addition of labile $[\text{W}(\text{THF})(\text{CO})_5]$ or $[\text{Au}(\text{C}_6\text{F}_5)(\text{THT})]$ (THT = tetrahydrothiophene) to this red solution failed to afford isolable ylide complexes upon workup, and no trapping experiments with organic electrophiles (*e.g.*, ketones) were attempted due to limited quantities of the arsolylum on-hand.

The remainder of the C_6D_6 reaction solution contained the expected $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ as the major cyclopentadienyl-containing species. Interestingly, $[\text{MoMe}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ is also observed, which speaks to the possible occurrence of radical reaction pathways, since the addition of NaI to [2a]OTf gave $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ (^1H NMR (acetone- d_6): $\delta_{\text{H}} = 5.88$ ppm *cf.* an authentic sample) and $\text{MeAsC}_4\text{Me}_4$ *exclusively*; the presence of a fleeting pentavalent As(v) species *i.e.*, $[\text{Mo}\{\text{AsMe}(\text{I})\text{C}_4\text{Me}_4\}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ which then dismutates to $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ and $[\text{MoMe}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$, is therefore discounted.

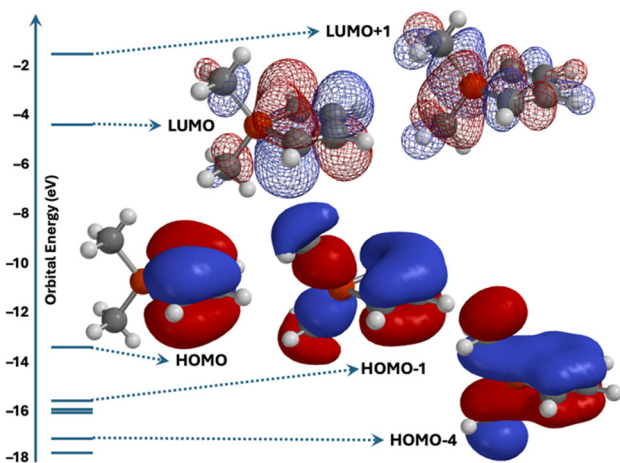


Fig. 7 Frontier orbitals of interest for the hypothetical dimethyl-arsolylum cation $[\text{Me}_2\text{AsC}_4\text{H}_4]^+$ (DFT: ω B97X-D/6-31G*/gas phase).

Pentavalent (λ^5) arsoles¹³ are a subject to which we will return in detail in a subsequent paper. Repeating the reaction in *n*-hexane solution followed by storage at -30 °C provides an abundance of crystalline specimens comprising no fewer than five molybdenum-containing compounds which were identified by X-ray diffraction. In addition to [4]I (Fig. 6), they are: (a) $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ (Fig. 8), which despite being a septuagenarian compound¹⁴ had not been previously structurally characterised; (b) $[\text{MoMe}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$, a similarly venerated organometallic,¹⁴ (c) *cisoid*- $[\text{MoI}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5-\text{C}_5\text{H}_5)]$ (*cisoid*-5, Fig. 8a), arising from carbonyl rather than arsole substitution, and (d) its isomer *transoid*- $[\text{MoI}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5-\text{C}_5\text{H}_5)]$ (*transoid*-5, Fig. 9b) as a co-crystallite with (e) the novel acyl complex *transoid*- $[\text{Mo}\{\text{C}(\text{O})\text{Me}\}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5-\text{C}_5\text{H}_5)]$ (6, Fig. 10).

Despite being first reported in 1956 by Wilkinson,¹⁴ and having been utilised as a synthon in a variety of settings in the interregnum,¹⁵ the crystal structure of red $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ would appear to have been neglected. It transpires however that the structure had in fact been previously determined, but incorrectly identified as the diamagnetic (*sic.*, d^3) compound $[\text{Mo}(\text{Te})(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ (CCDC 216750†). This was purported to arise from the reaction of $[\text{Mo}_2(\text{CO})_6(\eta^5-\text{C}_5\text{H}_5)_2]$ with diphenylditelluride and $[\text{nBu}_4\text{N}]\text{I}$,^{16a} but is clearly $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$. Understandably, molecular features are rather unexciting given the simplistic nature of the complex and only salient crystallographic aspects are noted here. A seven-coordinate molybdenum(II) centre is found which approximates a dis-

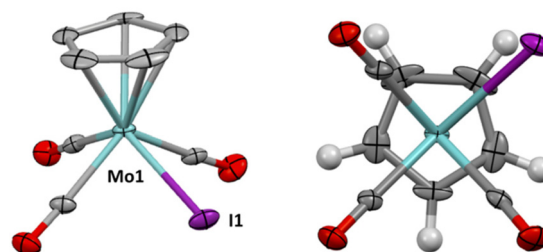


Fig. 8 Molecular structure of $[\text{MoI}(\text{CO})_3(\eta^5-\text{C}_5\text{H}_5)]$ in a crystal (50% displacement ellipsoids, most hydrogen atoms omitted).

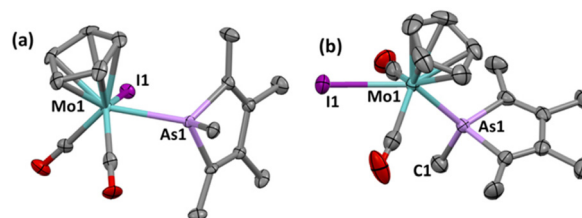


Fig. 9 Isomeric pentamethylarsole complexes. Molecular structures of (a) *cisoid*- $[\text{MoI}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5-\text{C}_5\text{H}_5)]$ (*cisoid*-5) in a crystal (one of two crystallographically unique molecules) and (b) *transoid*- $[\text{MoI}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5-\text{C}_5\text{H}_5)]$ (*transoid*-5) in a co-crystallite of (*transoid*-5)_{0.11}(6)_{0.89}. (50% displacement ellipsoids, methyl groups simplified and most hydrogen atoms omitted).

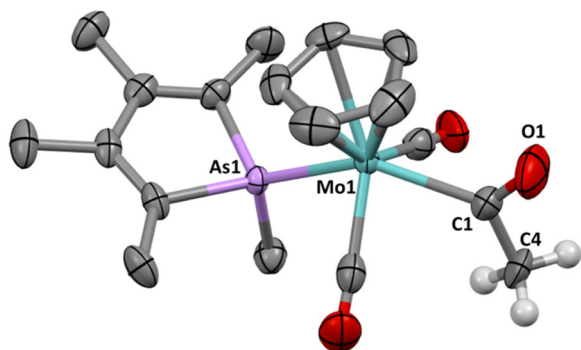


Fig. 10 Molecular structure of *trans*-[Mo{C(=O)Me}(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅)] (**6**) in a co-crystallite of (*trans*-**5**)_{0.11}(**6**)_{0.89}. (50% displacement ellipsoids, arsole methyl groups simplified and most hydrogen atoms omitted).

torted square-based pyramid, where the three carbonyls and the iodide ligand comprise the basal plane and the centroid of the cyclopentadienyl ring occupies the apical site. The Mo–I bond length of 2.8419(6) Å is typical among similar complexes,¹⁶ and the Mo–C bond *transoid* to the iodide (1.992(6) Å) is marginally shorter than the pair *cisoid* (mean 2.035(7) Å) due to the π-donor character of the halide. The unit cell (monoclinic *P*₂₁/*n*) contains four symmetry-related molecules which display two intermolecular H⋯I interactions (per molecule) of *ca.* 3.1 Å in length that likely assist with relative orientations during lattice formation. The yellow organometallic complex [MoMe(CO)₃(η⁵-C₅H₅)] first prepared by Wilkinson^{14a} was structurally characterised much later by Valente and co-workers^{14b} who sought to utilise it for the catalytic epoxidation of cyclic alkenes in the presence of *tert*-butylperoxide. The Mo–C(sp³) distance was 2.326(3) Å and no unusual intermolecular interactions were found.

Dark red *cisoid*-[MoI(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅)] (*cisoid*-**5**, Fig. 9a) crystallises in triclinic *P* $\bar{1}$ and the unit cell contains four molecules comprising two pairs of enantiomers, which differ in the relative position of the arsole ligand to the iodide (either to the “left” or “right”) when viewed along the molybdenum-cyclopentadienyl centroid axis. The pair of molecules within the asymmetric unit are crystallographically unique though interatomic distances and angles are statistically indistinguishable between the two entities. The molybdenum atom adopts the usual seven-coordinate geometry which approximates a square-based pyramid. The As→Mo dative bond measures 2.5640(6) (molecule **A**) and 2.5717(6) (**B**) Å and the Mo–I covalent bonds are unremarkable at 2.8524(4) (**A**) and 2.8442(4) (**B**) Å in length. The pentamethylarsole ligand lies approximately orthogonal to the vertical plane bisecting the Mo(CO)₃(η⁵-C₅H₅) moiety. Distances between arsole ring atoms are typical of σ-dative coordination complexes for this ligand (which are measurably different from [4]I above), with mean As–C_α, C_α–C_β and C_β–C_{β′} bond lengths of *ca.* 1.93, 1.35 and 1.50 Å, respectively.

The third set of red crystals contained two compounds in an unequal occupancy ratio which are apparently (or approxi-

mately) isosteric and superimposed within the lattice. They are *transoid*-[MoI(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅)] (*transoid*-**5**, minor component, 11% occupancy) and *transoid*-[Mo{C(=O)Me}(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅)] (*transoid*-**6**, major component, 89% occupancy). Refinement (including occupancy) led to a satisfactory structural model solution (*R*₁ = 0.0398), albeit with some eccentric displacement ellipsoids though no restraints/constraints to correct these were applied. The iodide complex is again presumed to arise from carbonyl rather than arsole substitution, and the simplest explanation for the occurrence of the acyl complex would superficially seem to involve migratory insertion of [MoMe(CO)₃(η⁵-C₅H₅)] (*vide infra*) trapped by free pentamethylarsole.

The two compounds co-crystallise in monoclinic *P*₂₁/*n* and in both species the pentamethylarsole ligand approximately straddles the (non-crystallographic) vertical symmetry plane of the Mo(CO)₂(η⁵-C₅H₅) centre with the As–methyl substituent projected between the pair of *cisoid* carbonyl ligands. Since the two complexes are superimposed within the crystal lattice, the positions of the Mo(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅) atoms are modelled as a weighted average of both and all interatomic dimensions therein are thus identical *viz.* the mean As→Mo dative bond for both complexes in *this particular crystal* is 2.5226(6) Å. All crystallographic uniqueness is observed in the region of the overlaid acyl and iodide substituents, with Mo–C(sp²), C=O and Mo–I distances of 2.230(9), 1.215(9) and 2.898(4) Å, respectively. The former two are typical¹⁷ whereas the latter is elongated compared the other Mo–I bond lengths observed previously (*ca.* 2.4–2.5 Å) since the presence of the arsenic atom in a *transoid* position is presumably a repulsive influence. It is noted that a *transoid* configuration appears to be the preferred condition for Group 6 acyl complexes of the form [M{C(=O)R}L(CO)₂(η⁵-C₅H₅)]¹⁸ with which [Mo{C(=O)Me}(MeAsC₄Me₄)(CO)₂(η⁵-C₅H₅)] also complies. For [MoIL(CO)₂(η⁵-C₅H₅)] it is reasonable to expect that, in general, ligands of superior π-acidity would favour the coordination site *transoid* to the iodide though pentamethylarsole is not expected to be particularly outstanding in this respect, possibly explaining why both *cisoid* and *transoid* isomers have crystallised. No general trend emerges from a survey of the literature and any *regio* preferences appear to be highly contextual *e.g.*, steric demands.¹⁹ In many cases the *cisoid* and *transoid* isomers interconvert depending on *inter alia* temperature and solvent polarity^{15f,20} and in others it is not possible to unambiguously distinguish isomers from the spectroscopic data reported.

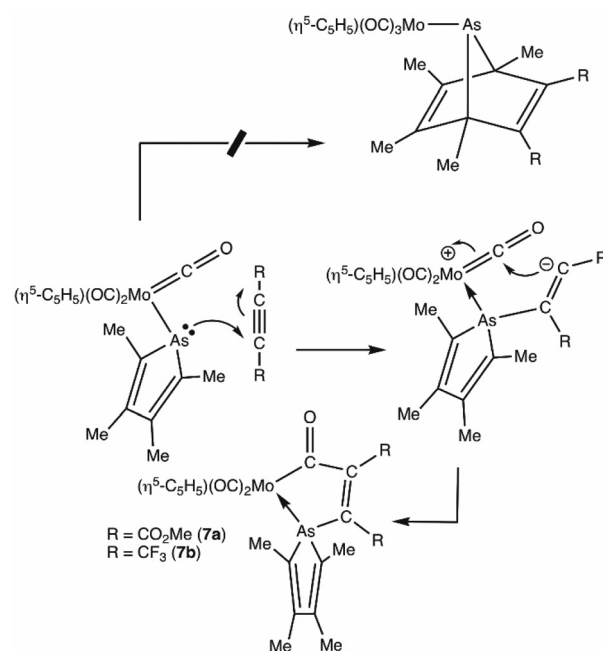
Acyl complexes of the mid-transition metals are well studied: their deliberate method of synthesis entails treatment of a metal carbonyl anion with an acyl halide or by migratory insertion of an alkyl complex,²¹ often in the presence of a Lewis base^{18a,b,20,22} although some Lewis acids have also been found to promote this process.²³ For acyl complexes prepared from the corresponding alkyl-carbonyl in the presence of a neutral two-electron ligand, the extraneous ligand is usually of reasonable basicity (*e.g.*, isocyanides, phosphines or phosphites) and weaker nucleophiles (amines, nitriles, arsines, stibines *etc.*) either provide the product in low yield²⁴ or afford

products of decarbonylation, especially for Group 6 centres. It is therefore intriguing that an acyl complex possessing an arsole ligand was observed, since (a) arsines appear less inclined to affect migratory insertion reactions upon exposure to $[\text{MoR}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$,²⁵ (b) the reaction was carried out at $-30\text{ }^\circ\text{C}$ whereas thermal impetus (generally $\gg 25\text{ }^\circ\text{C}$) is often required, and (c) the reaction was carried out in *n*-hexane medium, which is considered to disfavour the migration process, being unable to effectively stabilise the coordinatively unsaturated and dipolar transition state.^{22a} Attempts were made to deliberately synthesise $[\text{Mo}\{\text{C}(\text{O})\text{Me}\}(\text{MeAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ (**6**) by heating $[\text{MoMe}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ to $80\text{ }^\circ\text{C}$ in CD_3CN with one equivalent of $\text{MeAsC}_4\text{Me}_4$. The metal alkyl signals were unaffected and only gradual decomposition of the arsole was observed; a similar outcome was obtained with $\text{PhAsC}_4\text{Me}_4$, an arsole of superior thermal stability, wherein the spectrum was totally unchanged after heating. It is also noted that these arsoles did not proceed to carbonyl substitution products either (*i.e.*, *cisoid*- or *transoid*- $[\text{MoMe}(\text{RAsC}_4\text{Me}_4)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$, $\text{R} = \text{Me}, \text{Ph}$), speaking to their poor nucleophilicity. The presence of **6** among the crystalline products therefore remains inexplicable since the reaction conditions would be expected to disfavour formation of such a compound (*vide supra*); like the occurrence of $[\text{MoMe}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ in the mixture, it is possible that radical processes may be operative though not *via* any photochemical route since this reaction was performed in the dark.

Reactions with electrophilic alkynes

Both metal-complexed phosphole and arsole ligands are known to undergo $[4 + 2]$ cycloadditions upon treatment with dienophiles.^{26–28} For the former, this led to the formation of stable 9-phosphanorbornene and -norbornadiene complexes *en route* to the first examples of saturated phosphirane ($\text{RPC}_2\text{R}'_4$) and unsaturated phosphirene ($\text{RPC}_2\text{R}'_2$) complexes.²⁶ Voß and Schenk treated the Group 6 pentacarbonyl arsole complexes $[\text{M}(\text{RAsC}_4\text{Me}_4)(\text{CO})_5]$ ($\text{M} = \text{Cr}, \text{W}$; $\text{R} = \text{Me}, \text{tBu}, \text{Ph}$) with the electrophilic alkyne dimethylacetylene dicarboxylate (DMAD, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$) though only the corresponding tetramethyl-*ortho*-phthalate dimethylester was isolated and no 9-arsanorbornadiene complex was obtained.²⁷ Leung has, however, demonstrated the enantioselective $[4 + 2]$ cyclo-additions of alkenes to palladium-coordinated arsoles.²⁸ It was therefore of interest whether arsoles bearing metal substituents might enter into *pseudo*-Diels–Alder processes with activated alkynes.

The nucleophilic arsolyl **1a** reacts rapidly with a slight excess of DMAD in CH_2Cl_2 solution at ambient temperature and complete consumption of **1a** occurs within only a few minutes of mixing as confirmed by IR spectroscopy. Purification *via* column chromatography on Florisil® provided an air-stable, reddish-brown solid as the only isolable compound in good yield (85%). High-resolution mass spectrometry confirmed the formation of a 1 : 1 **1a**/DMAD cycloadduct ($m/z \approx 572.9797$) though both the ^1H NMR (C_6D_6) and IR data were *not* consistent with a C_s -symmetric $[4 + 2]$ cycloaddition 9-arsa-



Scheme 5 $[3 + 2]$ -cycloaddition of a σ -arsolyl complex **1a** with activated alkynes ($\text{R} = \text{CF}_3, \text{CO}_2\text{Me}$).

norbornadien-9-yl product of the form $[\text{Mo}\{\text{AsC}_6\text{Me}_4(\text{CO}_2\text{Me})_2\}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (Scheme 5).

Neither the arsolyl nor alkyne moieties eventuate in symmetrical environments: a pair of methyl ester (3.45, 3.23 ppm, relative integration 3 : 3) and trio of methyl (1.88, 1.59 and 1.54 ppm, relative integration 3 : 3 : 6) signals in the ^1H NMR spectrum, in addition to three equal intensity carbonyl resonances ($\delta_{\text{C}} = 263.2, 245.5$ and 234.7) indicate the molecule has no element of symmetry. The 9-arsanorbornadienyl formulation would allow a time-averaged molecular plane of symmetry on the ^{13}C NMR timescale through rotation around the Mo–As bond and may therefore be discarded. Furthermore, the solution IR spectrum (CH_2Cl_2) exhibits a ν_{CO} intensity profile that is *not* suggestive of a C_s -symmetric $\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ centre. Instead, only two terminal carbonyl modes are observed at $1962(\text{vs})$ and $1889(\text{s})\text{ cm}^{-1}$ in addition to a lower-energy absorption at $1732(\text{s})\text{ cm}^{-1}$ indicative of a ketonic carbonyl. A pair of medium-intensity methyl ester carbonyl absorptions are found at 1605 and 1580 cm^{-1} .

The compound crystallised from Et_2O at $-20\text{ }^\circ\text{C}$ and X-ray diffraction revealed its identity as a novel spirocyclic 3-(arsolyl) propenoyl chelate complex $[\text{Mo}\{\text{C}(\text{O})\text{CR}=\text{CRAsC}_4\text{Me}_4\}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{CO}_2\text{Me}$, **7a**). The *Z*-propenoyl linkage arises from insertion of a DMAD molecule into the region of space between the nucleophilic arsenic atom and an electrophilic *cisoid* carbonyl ligand, forming a new five-membered molybda-arsacyclopentenone (Scheme 5).

The molecular structure is shown in Fig. 11, and a proposed mechanism of formation is given in Scheme 4. Consistent with the nucleophilicity of the arsenic centre discussed above, the mechanism commences with DMAD acting as an electrophile towards arsenic, rather than as a dienophile to the arsolyl

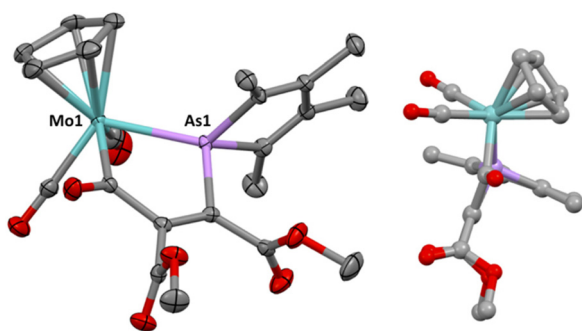


Fig. 11 The molecular structure of one enantiomer **7a** in a crystal (50% displacement ellipsoids, methyl and ester groups simplified and hydrogen atoms omitted, alternative enantiomer generated by $P\bar{1}$ crystallographic symmetry). Inset: Alternative perspective of the molecule.

butadiene component. It should be noted that a not dissimilar process has been suggested to occur in the reaction of triphenylarsine with DMAD, for which a somewhat questionable and yet to be substantiated, λ^5 -arsenole $\text{Ph}_3\text{AsC}_4(\text{CO}_2\text{Me})_4$ has been proposed to arise.^{29,30}

The cycloadduct crystallises in triclinic $P\bar{1}$ and a pair of symmetry-related enantiomeric molecules (Fig. 11) are found in the unit cell. The net result of the reaction with DMAD is the formation of a new Mo–C covalent bond and conversion of the Mo–As bond to a As→Mo dative interaction. Thus, the molecular structure of the spirocyclic product features a pair of vertex-sharing pentagons united at the deformed tetrahedral arsenic atom – their angle of intersection (defined by the separate mean planes of each five-membered ring) is nearly perpendicular at 87° . This indicative geometric parameter comes with some imprecision as only the arsole ring is approximately planar (envelope angle *ca.* 7°) whereas the molybda-arsacyclopentenone is puckered at the arsenic and acyl carbon atoms by *ca.* 20° . Reflecting the fact that all interatomic bonds within the ring are unique, the dimensions of the pentagonal metallacyclic system are expectedly distorted from the ideal such that the molybdenum atom is skewed toward the acyl carbon by over 0.25 \AA (Mo–C $2.244(2)$ vs. As→Mo $2.5110(2) \text{ \AA}$). The latter compares to the marginally longer As→Mo dative interaction of $2.5844(4) \text{ \AA}$ found in $[\mathbf{2a}]^+$ (Fig. 2). Ring-atom distances within the arsolypropenoyl chelate are typical of the individual bonding partners, comprising regular localised C=O, C–C, C=C and C–As covalent bonds. Reflecting the appreciable adjustment to bonding patterns surrounding the Mo(η) centre, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6) of **7a** reveals two resonances for the diastereotopic terminal carbonyl ligands, to low frequency of **1a** (263.2, 245.5 ppm) with the acyl carbonyl resonance at 234.7 ppm. The chemically unique methyl ester carbon signals appear at 167.1 and 159.9 ppm to slightly higher frequency of the propenoyl olefin carbon atoms at 161.0 (acyl-bound) and 149.7 (arsenic-bound) ppm. The arsole ring atoms are all inequivalent, manifest as four distinct signals in the range 146.5–132.9 ppm while the remaining cyclopentadienyl and methyl resonances are unremarkable.

Given the formation of **7a** from **1a** and DMAD, the generality of the reaction with respect to alkyne functionalisation was explored. Combining **1a** with hexafluorobut-2-yne (HFB, $\text{F}_3\text{CC}\equiv\text{CCF}_3$) in CH_2Cl_2 solution at -78°C followed by warming to ambient temperature was accompanied by a colour change from orange to a deep red, and purification by column chromatography on Florosil® provided the second example of a 3-(arsoly)propenoyl species, *viz.* $[\text{Mo}\{\text{C}(\text{=O})\text{CR}=\text{CRAsC}_4\text{Me}_4\}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ (R = CF_3 **7b**), in high yield (90%). Alkyne insertion is confirmed by comparison of IR, NMR and MS data with those for **7a** in addition to the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (C_6D_6) which confirmed the two chemically unique CF_3 groups ($\delta_{\text{F}} = -56.7, -59.1 \text{ ppm}$, $^5J_{\text{FF}} = 10.2 \text{ Hz}$). Single crystals of **7b** were grown by evaporation of a Et_2O solution at 0°C and the molecular structure, determined by X-ray diffraction, is shown in Fig. 12.

The complex crystallises in centrosymmetric monoclinic $P2_1/n$ and the centric unit cell therefore contains both enantiomers, though only one is shown in Fig. 12. The gross molecular configuration of **7b** is analogous to that of **7a** (Fig. 10) and most salient features of the latter are applicable to the former. Thus, the formal $[3 + 2]$ addition of one HFB molecule to the region between the arsenic atom and a *cisoid* carbonyl provides a new five-membered ring encompassing the arsolypropenoyl chelate ligand. The respective As→Mo and Mo–C bonds measure $2.5161(5)$ and $2.216(3) \text{ \AA}$, respectively, and the mean planes of the vertex sharing five-membered rings intersect at an angle more acute than in the previously discussed DMAD $[2 + 3]$ cycloadduct, approximately 78° , though a similar puckering of the molybda-arsacyclopentenone ring (*ca.* 17°) is measured.

The bright yellow/orange colours of **7a** and **7b** may be traced to primarily MLCT transitions from metal-based orbitals (HOMO–0,1,2) to unoccupied orbitals located primarily on the metallacycle (LUMO), the arsole (LUMO+1) and carbonyl ligands (LUMO+2) on the basis of computational analysis (TD-DFT: $\omega\text{B97X-D/6-31G}^*/\text{LANL2DZ}/\text{gas-phase}$) of **7b** (see ESI†).

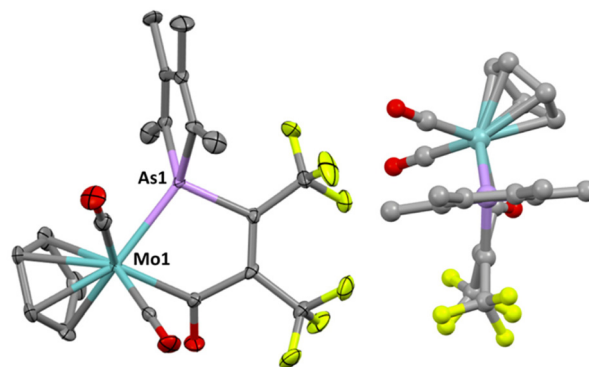


Fig. 12 The molecular structure of one enantiomer of **7b** in a crystal (50% displacement ellipsoids, methyl groups simplified and hydrogen atoms omitted, alternative enantiomer generated by crystallographic $P2_1/n$ symmetry).

In contrast to the facile replacement of pentamethylarsole by iodide from $[2a]^+$, the arsolylpropenoyl complexes were surprisingly resistant toward displacement of the arsenic donor: no reaction whatsoever was observed upon treatment of **7a** with an excess of PMe_3 , $P(OMe)_3$ or $tBuNC$ at elevated temperatures (C_6D_6 , 80 °C). The NMR spectrum of **7b** was unchanged after being sealed under an atmosphere of carbon monoxide for one week, and the addition of $[NO]PF_6$ to a CD_3CN solution of the same led to complete decomposition with gas evolution. No reaction was observed between **1a** and electron rich alkynes such as 2-butyne and diphenylacetylene, nor between $[2a]^+$ or $[MoAu(\mu-AsC_4Me_4)(C_6F_5)(CO)_2(\eta^5-C_5H_5)]$ (from **1a** and $[Au(C_6F_5)(THT)]^{2b}$) and DMAD. The addition of other typically dienophilic substrates such as *ortho*-benzyne (*via* the Kobayashi protocol³¹), tetracyanoethylene and *N*-phenylmaleimide did not afford similar spirocyclic cycloadducts (by mass spectrometry) and instead yielded chromatographically immobile compounds, except for the former which afforded a very small quantity of $[Mo_2(CO)_6(\eta^5-C_5H_5)_2]$. The course of these latter reactions was not reliably deduced from spectroscopic data.

In light of the above reactions between **1a** and DMAD or HFB, it is unsurprising that other transition metal arsenidos undergo analogous ring forming process with electron-poor alkynes: Davidson *et al.*, have treated the cacodyl complexes $[M(AsMe_2)(CO)_n(\eta^5-C_5H_5)]$ ($M = Fe, n = 2$; $M = W, n = 3$) with the same alkynes to produce the metallacycles $[M\{C(O)CR=CRAsMe_2\}(CO)_{n-1}(\eta^5-C_5H_5)]$ ³² and in this regard the behaviour of the AsC_4Me_4 ligand resembles that of a conventional arsenido ligand despite the nucleophilic diene function in combination with the demonstrated dienophilic proclivities of DMAD and HFB. Notably, a large excess of the alkyne was employed yet the arsole butadiene remained intact, even when the arsenic lone pair of electrons is already sequestered in $As \rightarrow M$ bonding to reinforce the diene (*cf.* aromatic elementole) character. Mathey has noted that the disubstituted phospholyl complexes $[W(PC_4R_2R')_2(CO)_3(\eta^5-C_5H_5)]$ ($R = H, R' = Me$; $R = Ph, R' = H$) are also reluctant to undergo $[4 + 2]$ cycloaddition reactions with dienophiles (despite the same phosphole rings entering into cycloaddition reactions when coordinated to $W(CO)_5$ ³³), instead yielding phospholylpropenoyl complexes.³⁴ Cullen has reported an arsinopropenoyl complex of rhenium(i) obtained by photolysis of $[Re_2(CO)_{10}]$ with the bis(arsino)butene $Z-Me_2AsC(CF_3)=C(CF_3)AsMe_2$, though the low yields discourage mechanistic conjecture.³⁵

Conclusions

The susceptibility of σ -arsolyl ligands towards electrophilic attack at arsenic has been demonstrated, recalling similar behaviour by more conventional arsolyl ligands devoid of the unsaturated elementole ring. This adds to the already documented propensity of σ -arsolyls to coordinate to extraneous Lewis-acidic metal centres.^{2b} Even reactions that might be expected to involve the 2,4-diene unit, *viz.* *pseudo*-Diels–Alder $[4 + 2]$ cycloadditions either fail or alternatively proceed again

via direct electrophilic attack at the arsenic. It remains to be seen if this is a specific feature of the $'Mo(CO)_3(\eta^5-C_5H_5)'$ metal centre or arsolyl substitution pattern chosen for study.

Experimental

Experimental protocols, instrumentation, crystallographic and computational methods are provided in the accompanying ESI.†

Author contributions

RMK was responsible for the design and execution of the experimental research, the acquisition and critical analysis of the characterisation data and compilation of the original draft. AFH was responsible for funding acquisition, project conceptualisation and administration, validation and refinements to the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data have been deposited at the CCDC under accession numbers 2145381–2145383, 2149526, 2145364, 2145367, 2145351 and 2145459 and can be obtained from <https://www.ccdc.cam.ac.uk>.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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