Arsolyl-supported intermetallic dative bonding†

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The first examples of late transition metal \(\eta^5\)-arsolyl complexes \([Co(CO)](L)(\eta^5-AsC_4R_4)\) \((L = CO, P(O)Me_3); R = Ph, Me, Et, SiMe_3; R’ = Ph, H, Me, Et, Me) serve as ditopic donors to extraneous metal centres \((M = Pt^{II}, Au^{I}, Hg^{I})\) through both conventional As \(\rightarrow M\) and polar-covalent (dative) Co \(\rightarrow M\) interactions.

Heating \([Co_2(CO)_8]\) and a selection of As-phenyl arsoles \((1a-e, Scheme 1)\) in reflux THF or \(n\)-hexane provides the highly air-sensitive arsolyl complexes \([Co(CO)](\eta^5-AsC_4R_4)\) \((2a-e)\) in modest yields following strictly anaerobic chromatography. Efforts to increase the isolated yields of \(2a-e\) with extended reaction times or increased reaction temperatures were unsuccessful, however slightly increased yields were obtained by instead employing the more reactive As-chloro arsoles (see ESI†). The precise fate of the As-substituent during these reactions was not evident from the significant quantities of intractable materials also produced. The cleavage of an As-Ph bond from an arsole has on one previous occasion been observed in the reaction of \([Mn_2(CO)]\) with \(PhAsC_4Me_2H_2\), albeit under rather more forcing conditions \((150 \, ^\circ C, 4\) hours). Sub-optimal yields notwithstanding, the syntheses of \(2a-e\) were highly reproducible, affording complexes \(2a\) and \(2b\) as orange solids or \(2c-e\) as dark orange-red liquids at ambient temperature; the latter group underwent substitution with trimethylphosphite in toluene at 100 °C to provide the bright orange crystalline complexes \([Co(CO)](P(O)Me_3)\)(\(\eta^5-AsC_4R_4)\) \((2f-h)\) in high yield.

Selected spectroscopic data for \(2a-e\) and other germane cobalt(i) dicarbonyl complexes are presented in Table 1. We note that \(v_CO\) frequencies for \(2a-e\) fall between those for \([Co(CO)](\eta^5-C_5H_5)\) and \([Co(CO)](\eta^5-C_5Me_5)\), being comparable to those for \(\eta^5\)-phospholyl cobalt dicarbonyl complexes.
reported by Mathey. The $^{13}$C{1H} NMR shifts for the CO ligands in 2a–e mirror the trends in $\nu_{\text{CO}}$ frequencies with a gradual shift to higher frequency and are not dissimilar to those for [Co(CO)$_2$(η$^5$-C$_5$R$_5$)] ($R = \text{H}, 204.7; \text{R} = \text{Me}, 207.9$ ppm) and [Co(CO)$_2$(η$^5$-PC$_5$/Bu$_5$H$_5$)] (204.0 ppm). Comparison of $^{13}$C{1H} NMR data of the ring-carbon nuclei to those of the corresponding free arsoles 1a–e (ESI†) reveals a shift to low frequency of 20–30 ppm. The molecular structures of 2a, 2b, 2f, and 2h were crystallographically determined, with two representative examples, 2a and 2f, depicted in Fig. 1 (for 2b and 2h see ESI†).

The structural models for 2a, 2b, 2f and 2h all confirm the targeted η$^5$-arsolyl coordination. In 2a and 2f the ligands are almost symmetrically disposed with respect to the vertical plane which bisects the η$^5$-arsolyl ring, whereas for 2b and 2h these are rotated to a position slightly offset from the arsenic-ring centroid vector (ESI†). Consistent with the difference in the covalent radii of carbon (0.76 Å) and arsenic (1.19 Å), the latter is in each case very slightly displaced (3–5°) from the mean plane defined by the heterocyclic carbon atoms, though less than found in the free arsoles (1a: 10.2°; 2b: 7.10°). The geometry of the metal and η$^5$-arsolyl rings in 2a, 2b, 2f and 2h are of a distorted pentagonal pyramid. The C$_{ars}$-As$_{ars}$ angles at the arsenic vertices are significantly contracted (84–87°) from that of an idealised pentagon (108°) while the remaining C–C–C angles are in the range 111–114°, and comparable to those found in [Co(CO)$_2$(η$^5$-C$_5$R$_5$)] ($R = \text{Me}, \text{Ph}, \text{CH}_2\text{Ph}$). The results of computational interrogation of the model ‘parent’ compound [Co(CO)$_2$(η$^5$-As$_4$H$_4$)] (2$\text{As}_4$) (DFT:0.997X-D/6-31G*;LANL2DZ; ESI†) are summarised in Fig. 2 alongside those for [Co(CO)$_2$(η$^5$-C$_5$H$_5$)] (2$_{\text{CH}}$), and the hypothetical pnictogenyl analogues [Co(CO)$_2$(η$^5$-AC$_4$H$_4$)] (A = N$_2$; P$_2$; Sb$_2$$_{\text{Sb}}$). The HOMO–1 is in all cases substantially derived from the Co-d$_z$ orbital and readily corroborets the known nucleophilic behaviour of 2$_{\text{CH}}$. For 2$_{\text{CH}}$ this is, however, effectively the only orbital that is geometrically disposed to allow the complex to function as a Lewis base since the HOMO is involved with cyclopentadienyl binding. This is also the case with the HOMO of the pnictogenyl examples however the orbital substantially protrudes radially from the ring. The HOMO–1 involves substantial contribution from the pnictogen orbital such that both the HOMO and HOMO–1 (and also HOMO–2) contribute to a prominent region of electron density localised over these atoms which is reflected in the electrostatic potential map for 2$\text{As}_4$ and

### Table 1

| Entry | Complex | $^{13}$C $\delta_{a}^{c}$ | $^{13}$C $\delta_{p}^{c}$ | $^{13}$C $\delta_{\text{CO}}^{a}$ | $\nu_{\text{CO}}^{b}$ (sym) | $\nu_{\text{CO}}^{b}$ (asym) | $k_{\text{CO}}^{c}$ |
|-------|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2a    | Co(CO)$_2$(η$^5$-As$_4$H$_4$) | 173.2 | 135.1 | 203.8 | 2026 | 1978, 1970 | 16.13 |
| 2b    | Co(CO)$_2$(η$^5$-As$_4$H$_4$) | 185.1 | 94.9 | 203.0 | 2032 | 1985, 1976 | 16.23 |
| 2c    | Co(CO)$_2$(η$^5$-As$_4$Me$_4$) | 118.9 | 113.1 | 205.1 | 2019 | 1967 | 16.02 |
| 2d    | Co(CO)$_2$(η$^5$-As$_4$Et$_4$) | 124.8 | 118.6 | 205.3 | 2017 | 1965 | 15.99 |
| 2e    | Co(CO)$_2$(η$^5$-As$_4$(SiMe$_3$)$_2$Me$_2$) | 122.2 | 119.8 | 204.5 | 2015 | 1962 | 15.95 |
| 2f    | Co(CO)$_2$(η$^5$-As$_4$(SiMe$_3$)$_2$Me$_2$) | 114.3 | 109.8 | 206.8 | 1947 | 15.39 |
| 2g    | Co(CO)$_2$(η$^5$-As$_4$(SiMe$_3$)$_2$Me$_2$) | 124.4 | 115.3 | 207.3 | 1945 | 15.36 |
| 2h    | Co(CO)$_2$(η$^5$-As$_4$(SiMe$_3$)$_2$Me$_2$) | 118.7 | 116.1 | 205.5 | 1941 | 15.30 |

* C$_6$D$_6$ solution unless otherwise stated, ppm downfield from SiMe$_4$, 25 °C; the labels $\alpha$ and $\beta$ refer to ring-carbon positions with respect to the heteroatom (where applicable). * $n$-Hexane solution unless otherwise stated, cm$^{-1}$, 25 °C. * Cotton–Kraihanzel force constant in N cm$^{-1}$. * Resolution of the doubly degenerate E vibrational mode is observed in $n$-hexane for these complexes cf., $\nu_{\text{CO}}$ (CH$_2$Cl$_2$): 2a 2022, 1963 cm$^{-1}$; 2b 2027, 1972 cm$^{-1}$. * CDC$_3$ solution, 25 °C. * Cyclohexane solution.

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Fig. 1 Molecular structures of (a) 2a and (b) 2f (50% displacement ellipsoids, arsenolyl ring and phosphite substituents simplified). Selected distances [Å] and angles [°]: 2a As1–Co1 2.427(4), As1–C3 1.900(1), C3–C4 1.443(3), C4–C5 1.427(3), C5–C6 1.439(3), C6–As1 1.915(2), Co1–C1 1.746(3), Co1–C2 1.747(3), C3–As1–C6 84.52(8), As1–C5–C4 114.32(4), C3–C4–C5 113.65(2), C4–C5–C6 112.84(2), C5–C6–As1 114.38(1), C1–Co1–C2 90.82(2); 2f As1–Co1 2.408(3), As1–C5 1.910(3), C5–C6 1.430(4), C6–C7 1.423(4), C7–C8 1.427(5), C8–As1 1.903(3), Co1–C1 1.719(3), Co1–P1 2.097(9), C5–As1–C8 84.12(1), As1–C5–C6 114.25(2), C5–C6–C7 113.30(3), C6–C7–C8 113.47(3), C7–C8–As1 114.56(2), C1–Co1–P1 93.49(1). (c) Intersection of C5–C6–C7–C8 (blue) and P1–Co1–C1–C2 (red) planes for 2f at 89.7° with As, C5, C6, C7, C8 centroid in green.
the condensed Fukui functions for both arsenic and cobalt (Fig. 2 inset). Furthermore, on descending group 15, the pnictogen A–P– orbital increasingly contributes and this is accompanied by a monotonic increase in the energy the HOMO, HOMO–1 and HOMO–2 orbitals which should manifest as an increase in the basicity of not only the metal but also the pnictogen. This is intriguingly counterintuitive in that the basicity, nucleophilicity and strength of pnictogen coordination generally decreases for simple pnictanes AR₃ traversing from P to Sb.⁴⁰ Compared to phospholyl and arsølyl complexes, η⁵-stibolyl complexes are rarer still, being limited to three ferrocene analogues, but clearly worthy of further study, not least because of the onset of secondary bonding for the heavier pnictogens.¹³

To explore the possibility of metal–metal bond formation, the representative 2c was chosen, commencing with mercuric chloride by analogy with the prototypical and monomeric adduct [Co(HgCl₂)[CO]₂(η⁵-C₄H₄)].¹² The reaction of 2c with HgCl₂ in acetone rapidly results in precipitation of the poorly soluble yellow dimer [2c–HgCl₂(μ-Cl)]₂ (3) in high yield (Scheme 2 and Fig. 3).

The dimeric formulation follows from HR-ESI-MS data, which are devoid of ions due to dissociated 2c, in addition to crystallographic analyses of two isomers that differ in the μ-η⁵-arsonyl rings adopting mutually syn or anti positions with respect to the rhomboidal Hg₂[μ-Cl₂] core. Thus, yellow needles of anti-3 (major) and orange prisms of syn-3 (minor) slowly crystallise together from solutions of 3 in acetone stored at −30 °C.

One half of each of the dimeric structures of both anti-3 and syn-3 in the solid state is crystallographically unique due to the centre of the Hg₂[μ-Cl₂] unit coinciding with either an inversion centre (anti-3 in P2₁/n) or twofold rotation axis (syn-3 in C2/c). The coordination polyhedra of the Hg¹¹ atoms are strikingly different in each isomer: anti-3 features severely distorted trigonal bipyramidal mercury with the arsenic and cobalt atoms

![Scheme 2](image-url) Bridge-assisted formation of dative bonds from cobalt to gold(l), mercuryl(l) and platinum(l). (i) HgCl₂. (ii) cis-[Pt(C₆F₅)₂(hex)] (hex = 1,5-hexadiene). (iii) [Au(C₆F₅)(THT)] (THT = tetrahydrothiophene).

![Fig. 3](image-url) The molecular structures of (a) syn-3 and (b) anti-3 (methyl groups simplified, 50% displacement ellipsoids). Selected distances [Å] and angles [°]: (a) syn-3: As₁–Hg₁ 2.7268(9), Co₁–Hg₁ 2.6201(3), Hg₁–Cl₁ 2.491(2), Hg₁–Cl₂ 2.598(2), Hg₁–Cl₂¹ 2.708(2), As₁–Hg₁–Cl₁ 55.86(3), Hg₁–Cl₁–Hg₂ 91.87(6), Cl₂–Hg₁–Cl₂ 87.62(6), Cl₁–Hg₁–Cl₂ 100.71(6). (b) Anti-3: As₁–Hg₁ 2.6334(6), Co₁–Hg₁ 2.6702(9), Hg₁–Cl₁ 2.390(1), Hg₁–Cl₂ 2.778(1), Hg₁–Cl₂¹ 2.777(1), As₁–Hg₁–Co₁ 56.27(2), Hg₁–Cl₂–Hg₂ 84.37(4), Cl₂–Hg₁–Cl₂¹ 95.63(4), Cl₁–Hg₁–Cl₂ 100.59(5). i = crystallographic inversion centre.
assuming pseudo-axial and -equatorial positions, respectively (\(\tau_5 = 0.89\)), whereas for syn-3 the more sterically congested mercury geometry more closely approaches a square-based pyramid (\(\tau_5 = 0.62\)) with the non-bridging chlorides occupying the eclipsing apices. The As–Hg bond distances are somewhat shorter by ca. 0.1 Å in anti-3 (2.633(6) Å) than syn-3 (2.727(9) Å), while the Co–Hg bond distances of 2.670(9) Å (anti) and 2.620(1) Å (syn) are essentially equivalent within crystallographic precision limits. The latter pair are somewhat longer than the sum of covalent radii for the individual elements (2.58 Å) and the separation (2.578(4) Å) observed for \([Co(HgCl_2)](-CO)\text{[\(\eta^2-C_3H_5\)]}_4\) by virtue of the increased coordination number at mercury. The slight elongation of the Co → Hg interaction here is almost certainly a geometric compromise to accommodate the Hg\(^{II}\) centre within the disparate coordination spheres of the As\(^{III}\) and Co\(^{I}\) donors, rather than indicating any noteworthy electronic phenomena beyond non-directional spodumene bonding.\(^{14}\) From a valence-bond perspective, 2c may be considered to serve as a neutral, 4-electron bidentate ligand with a somewhat narrow bite-angle (ca. 55°–56°). Solution infrared data for each isomer (after manual separation of crystals) resulted in spectra identical to that of the bulk sample of \([Hg(CF_3)_2]\) nor \([Hg(C_6F_5)_2]\) provided any evidence of detectable formation.

Further exemplifying the bidentate nature of 2c, combination with one equivalent of \([Au(C_6F_5)_2](THT)\) (THT = tetrahydrothiophene) leads to the isolation of a yellow solid of deceptively simple composition “2c–Au(C_6F_5)\(_2\)” that is actually the salt \([2c]_2Au[[Au(C_6F_5)_2]]\) (5, Fig. 5). The crystal structure of 5 reveals bidentate coordination of two 2c units to a Au\(^+\) cation with near to coplanar coordination of the Co and As donors (Au sits 0.22 Å above the Co\(_2As_2\) mean plane). The 2c ‘ligands’ are}

Fig. 4 The molecular structure of 4 (methyl and pentfluorophenyl groups simplified. 50% displacement ellipsoids. Pt TBPY-5-12-C enantiomer in non-centrosymmetric \(P2_12_12_1\) space group). Selected distances [Å] and angles [°]: As1–Pt1 2.5185(8), Co1–Pt1 2.3996(1), Pt1–C12 2.0533(8), Pt1–C18 2.0777(7), As1–Pt1–Co1 53.04(3), As1–Pt1–C18 169.58(2), Co1–Pt1–C18 137.24(2).

Fig. 5 The molecular structure of 5 (methyl and pentfluorophenyl groups simplified and hydrogen atoms omitted for clarity. Four crystallographically independent molecules in the unit cell. 50% displacement ellipsoids). Selected distances [Å]: As1–Au1 2.5215(6), As2–Au1 2.5205(6), As1–Au2 3.1660(6), Co1–Au1 2.6793(9), Co2–Au1 2.6731(8). Selected angles [deg]: As1–Au1–Co1 57.89(2), As2–Au1–Co2 57.67(2), As1–Au1–As2 178.99(2), Co1–Au1–Co2 167.70(3). (a) View orthogonal to the \(b\)-axis showing extended chain of \(\cdots Au\_As\_Au\_As\_\cdots\) interactions (3.0746(6)–3.2122(6) Å).
asymmetrically disposed about the Au⁺ cation, being transposed and offset by ca. 22° when viewed along the As1–Au1–As2 vector. The As–Au distances are equivalent (mean 2.525 Å), with slightly longer Co–Au distances (mean 2.650 Å). The unit cell of 5 contains four crystallographically independent \([2e_{2}·Au]([Au(C_{6}F_{5})_{2}]_{2})\) pairs (ESI) with extended packing of loosely parallel columns of alternating \([2e_{2}·Au]^{+}\) cations and \([Au(C_{6}F_{5})_{2}]^{-}\) anions. The nature of their arrangement differs slightly between pairs, with notably short As–As (Löwdin bond orders As–As 0.75/0.41) (detailed in the ESI) returns core geometries close to those of 4 and the cation of 5. This analysis reveals molecular orbitals of interest (see ESI Fig. S12 and HOMO vector). The As pairs, with notably short As–As interactions (between the arsyl arsenic and \([Au(C_{6}F_{5})_{2}]^{-}\) gold atoms). These distances are, however, not equal, and capriciously vary between 3.074(6) Å (shortest) and 3.2122(6) Å (longest).

Computational interrogation \(\omega^{b97X-X/6-31G*/LANL2DZ}\) of the model complexes \([CoPt(\mu-AsC_{6}H_{4})(CO)_{4}](CF_{3})_{2}\) (4’) and \([Co_{2}Au(\mu-AsC_{6}H_{4})(CO)_{4}](CF_{3})_{2}\) (5’) (detailed in the ESI) returns core geometries close to those of 4 and the cation of 5. This analysis reveals molecular orbitals of interest (see ESI Fig. S12–S14) that account for the geometrical features of note. For 4’, the HOMO and HOMO–7 comprise significant overlap of the Co–d2 orbital with platinum, supporting a Co → Pt description (Löwdin bond orders As–Pt/Co–Pt = 0.75/0.41). For 5’ not only does the HOMO–16 adhere to the view of dative Co → Au bonding (Löwdin bond orders As–Au/Co–Au = 0.78/0.56), but an orbital (HOMO–20) has a topology suggestive of the arsnyl arsenyl serving as a π-acceptor from gold, a feature also present in the MO scheme for 4’. Furthermore, the LUMO which has substantial arsenic character would appear to account for the association of the \([Au(C_{6}F_{5})_{2}]^{-}\) anion at this point which underpins the extended polymeric assembly, though it is unlikely that this persists in solution.

**Conclusions**

The first (eight) examples of late transition metal 1e⁻-arsoyl complexes have been obtained with one example being then employed to explore the possibility of both the metal and arsenic serving as donors to PtII, AuI and HgII centres. Although the individual interactions might appear weak, when both act in concert novel bridge-assisted heterometallic assemblies arise with intriguing features.

**Data availability**

Crystallographic data for structurally characterised compounds have been deposited at the Cambridge Crystallographic Data Centre under CCDC 2130783–2130790 and can be obtained from [https://www.ccdc.cam.ac.uk](https://www.ccdc.cam.ac.uk). Spectroscopic data for all new compounds are provided in the ESI accompanying this paper ([https://doi.org/10.1039/d2sc01200f](https://doi.org/10.1039/d2sc01200f)).

**Author contributions**

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

**Conflicts of interest**

There are no conflicts to declare.

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