Arsaalkyne coupling reactions: synthesis, crystal and molecular structures of the first 1,3-diarsacyclobutadiene and 1,2-diarsetane complexes

Matthew D. Francis,[a] David E. Hibbs,[b] Michael B. Hursthouse,[b] Cameron Jones*[a] and K. M. Abdul Malik[b]

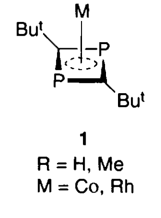
[a] *Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea, UK SA2 8PP*

[b] *EPSRC Crystallography Centre, Department of Chemistry, University of Wales, Cardiff, PO Box 912, Park Place, Cardiff, UK CF1 3TB*

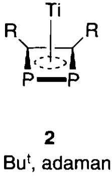
Treatment of the arsaalkyne $As{\equiv}C(C_6H_2Bu^t{}_3\text{-}2,4,6)$ with $[W(CO)_5(thf)]$ affords the compounds $[\{W(CO)_5\}_2\{1,3\text{-}\eta^1\text{-}As_2C_2(C_6H_2Bu^t{}_3\text{-}2,4,6)_2\}]$ 5 and $[\{W(CO)_5\}_2\{1,2\text{-}\eta^1\text{-}As_2C_2H_2(C_6H_2Bu^t{}_2CMe_2CH_2)_2\}]$ 6 which represent the first structurally characterised examples of 1,3-diarsacyclobutadiene and 1,2-diarsetane complexes respectively.

The debate over the geometry of the parent, anti-aromatic cyclobutadiene was laid to rest some time ago with the conclusion that it is rectangular with localised C–C double bonds.[1] Although only a transient species, it can be stabilised by substitution with sterically demanding groups, whilst retaining its rectangular geometry.[1] Theoretical studies have suggested that stabilisation can also be effected *via* substitution of one or more ring carbons with a group 15 element.[2] This has been tested in practice with the versatile phosphaalkyne ligand ($P{\equiv}CBu^t$) which readily dimerises at transition-metal centres to give either 1,3- or 1,2-diphosphacyclobutadiene complexes, *e.g.* **1** and **2**, in which the P–C double bonds are fully or partially delocalised.[3] In both these complex types the rings can be thought of as accepting two electrons from the metal centre and thus existing as aromatic dianions. To date there are no reported examples of either free or solely η^1-coordinated λ^3,λ^3-diphosphacyclobutadienes, though the former have been predicted as intermediates in an impressive array of organic cage and polycyclic compounds.[4]

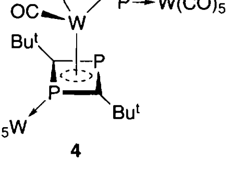
It is not surprising that the expanding field of diphosphacyclobutadiene chemistry has not been extended to diarsacyclobutadienes, presumably because of the instability inherent in low-coordination arsenic compounds. However, the organometallic chemistry of the only thermally stable arsaalkyne, *viz* $As{\equiv}C(C_6H_2Bu^t{}_3\text{-}2,4,6)$ **3**, has been recently initiated[5] with the finding that arsaalkynes behave similarly to phosphaalkynes, and therefore have potential as building blocks in the synthesis of diarsacyclobutadienes. With this in mind we decided to examine the reactivity of **3** with metal carbonyls in light of a recent report detailing the product of the reaction between $P{\equiv}CBu^t$ and $[W(CO)_5(thf)]$, *viz.* **4**.[6] Interestingly, **3** displays different reactivity to $P{\equiv}CBu^t$, which we report herein as giving rise to (*i*) the first examples of coupling reactions derived directly from arsaalkynes, (*ii*) the first 1,3-diarsacyclobutadiene, η^1-bonded to two metal fragments **5** and (*iii*) the first structural characterisation of 1,2-diarsetane complex **6**.



1
R = H, Me
M = Co, Rh



2
R = Bu^t, adamantyl



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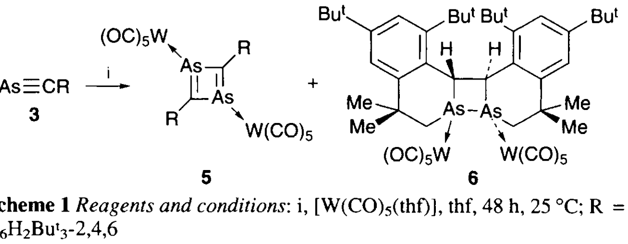
The reaction of **3** with $[W(CO)_5(thf)]$ at room temperature over 48 hours resulted in the low-yield formation of the red complex **5** (6% yield, mp 154 °C)[†] and the yellow complex **6** (9% yield assuming analytical purity, *vide infra*) (Scheme 1) which were purified by column chromatography (kieselgel, hexane) and recrystallisation from hexane. The low yields of **5** and **6** were largely due to the majority of **3** being returned unreacted after chromatographic work up. Surprisingly, efforts to increase the yields with more vigorous reaction conditions did not lead to a more complete reaction.

The molecular structure of **5** (Fig. 1)[‡] is centrosymmetric and thus displays a planar four-membered ring with a distorted rectangular geometry [C(7)–As(1)–C(7′) 85.8(7)°, As(1)–C(7)–As(1′) 94.2(7)°] that appears to contain fully localised As–C double [As(1)–C(7) 1.78(2) Å] and single [As(1)–C(7′) 2.01(2) Å] bonds. The former are slightly shorter than normally seen for As–C double bonds {*e.g.* 1.821(2) Å in $[(C_5H_5)Fe(CO)_2As{=}C\text{-}$



Scheme 1 *Reagents and conditions*: i, $[W(CO)_5(thf)]$, thf, 48 h, 25 °C; R = $C_6H_2Bu^t{}_3\text{-}2,4,6$

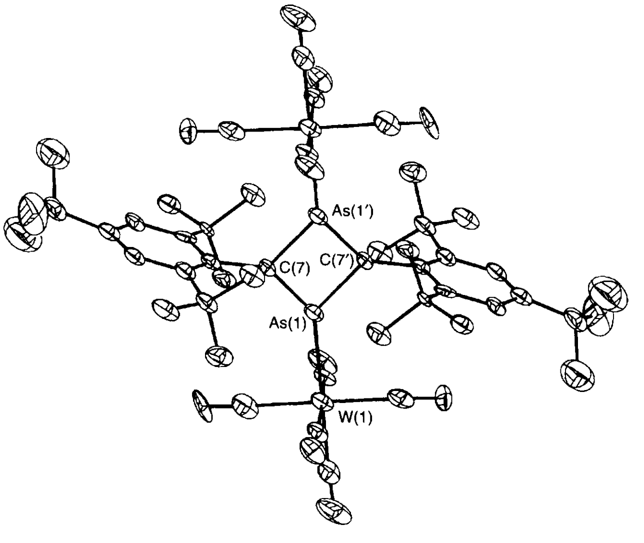


Fig. 1 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): As(1)–C(7) 1.78(2), As(1)–C(7′) 2.01(2), As(1)–W(1) 2.535(2), C(7)–As(1)–C(7′) 85.8(7), As(1)–C(7)–As(1′) 94.2(7), W(1)–As(1)–C(7) 140.7(6), W(1)–As(1)–C(7′) 133.5(4).

$Bu^t(OSiMe_3)]$[7] } but compare well with the theoretical value for the parent arsaalkene (1.770 Å[8]). The latter are slightly longer than the average As–C single bond length of 1.96 Å.[9] It is noteworthy that the As(1)–As(1′) distance [2.783(4) Å] is well within the sum of the van der Walls radii (4.00 Å) for two arsenic centres. The As–W bond lengths [2.535(2) Å] in **5** are in the normal range and are similar to those found in **6** (2.588 Å mean).

Compound **6** is a chiral, pentacyclic system with four optically active centres that crystallises as a racemic mixture of the (*S*,*S*,*R*,*R*) and (*R*,*R*,*S*,*S*) enantiomers. The molecular structure of the (*S*,*S*,*R*,*R*) enantiomer (Fig. 2)§ exhibits a central, non-planar four-membered ring (As–C–C 100.2° mean, C–As–As 78.7° mean) which is coordinated to two $W(CO)_5$ fragments. All the As–C (1.964 Å mean) and As(1)–As(2) [2.418(2) Å] bond lengths are close to the norms (1.96 and 2.45 Å respectively) expected for these interactions.[9]

Spectroscopic data† for **5** are as would be expected for it retaining its solid-state structure in solution. Unfortunately, however, the ^1H NMR spectrum of **6** proved more difficult to interpret. It is believed this arises due to a mixture of diastereoisomers of **6**, or other products, that coincidentally have the same column retention time under the chromatographic conditions employed in this study.

With regard to a mechanism for the formation of **5** it seems likely that the arsaalkyne initially forms a 1 : 1 complex with the $W(CO)_5$ fragment. Our prior studies[5] with **3** suggest that this fragment should be ligated η^2 to the As–C triple bond. However, the steric bulk of the 2,4,6-tri-*tert*-butylphenyl ligand may force the fragment to bond η^1 to the high s-character arsenic long pair,[10] or be in equilibrium between the two modes. Finally a head-to-tail [2 + 2] cycloaddition reaction between two $[W(CO)_5\{\eta^1\text{-AS}{\equiv}C(C_6H_2Bu^t_3\text{-}2,4,6)\}]$ **7** molecules would lead to **5**. Presumably, the formally anti-aromatic four-membered ring in **5** is stabilised by the considerable steric protection afforded by the presence of two $C_6H_2Bu^t_3$-2,4,6 and $W(CO)_5$ units.

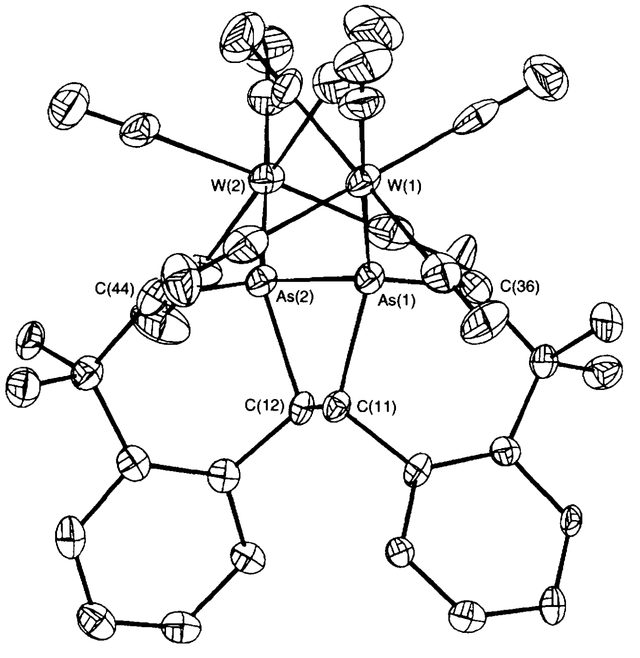


Fig. 2 Molecular structure of **6** (*tert*-butyl groups omitted for clarity). Selected bond lengths (Å) and angles (°): As(1)–As(2) 2.418(2), As(1)–C(11) 1.968(9), As(2)–C(12) 1.980(9), As(1)–C(36) 1.962(10), As(2)–C(44) 1.944(10), As(1)–W(1) 2.589(1), As(2)–W(2) 2.587(1), C(11)–C(12) 1.553(13), W(1)–As(1)–C(11) 127.3(3), W(1)–As(1)–As(2) 128.32(5), W(1)–As(1)–C(36) 125.0(3), As(1)–C(11)–C(12) 100.8(6), W(2)–As(2)–C(12) 127.9(3), W(2)–As(2)–As(1) 126.23(5), W(2)–As(2)–C(44) 124.5(3), As(2)–C(12)–C(11) 99.6(5).

There are several possible routes to **6**, the most likely of which involves a head-to-head [2 + 2] cycloaddition of two molecules of **7** to yield a 1,2-diarsacyclobutadiene complex. The resulting steric buttressing between the two $C_6H_2Bu^t_3$-2,4,6 groups could then force one *tert*-butyl group from each aryl ligand into close contact with an arsenic centre. An insertion of the arsenic centre into a C–H bond of this group, followed by a hydrogen migration would yield **6**. Similar migrations of a hydrogen atom from one carbon arom to another *via* a low-coordinate phosphorus centre have been previously observed in systems employing the $C_6H_2Bu^t_3$-2,4,6 ligand.[11]

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Footnotes

† *Spectroscopic data* for **5**: ^1H NMR (250 MHz, C_6D_6, 298 K, $SiMe_4$) δ 1.31 (s, 18 H, Bu^t), 2.11 (s, 36H, Bu^t), 7.52 (s, 4H, Ar); ν(CO)/cm^{-1} 2074m, 1964s, 1954s.

‡ *Crystal data* for **5**: $C_{48}H_{58}As_2O_{10}W_2$, M = 1312.48, triclinic, space group $P\bar{1}$, a = 11.191(4), b = 11.312(5), c = 11.403(3) Å, α = 99.71(2), β = 101.33(2), γ = 113.09(2)°, U = 1252.8(8) Å^3, Z = 1, D_c = 1.74 g cm^{-3}, $F(000)$ = 640, μ = 59.51 cm^{-1}, 278 parameters, crystal size 0.30 × 0.22 × 0.16 mm, Mo-Kα radiation (λ = 0.71069 Å), 150(2) K.

§ *Crystal data* for **6**: $C_{48}H_{58}As_2O_{10}W_2$, M = 1312.48, monoclinic, space group $P2_1/n$, a = 11.192(4), b = 23.426(5), c = 19.264(3) Å, β = 91.300(6)°, U = 5050(2) Å^3, Z = 4, D_c = 1.726 g cm^{-3}, $F(000)$ = 2560, μ = 59.06 cm^{-1}, 575 parameters, crystal size 0.24 × 0.20 × 0.18 mm, Mo-Kα radiation (λ = 0.71069 Å), 150(2) K.

All crystallographic measurements were made using a FAST area detector diffractometer. Both structures were solved by direct methods and difference synthesis and refined on F^2 by full-matrix least squares using all unique data. In both cases, all non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Final wR (on F^2) and R (on F) were 0.1155 and 0.1197 for **5**; 0.1269 and 0.0693 for **6** for all data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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