ORGANOMETALLICS

As-As Bond Formation via Reductive Elimination from a Zirconocene Bis(dimesitylarsenide) Compound

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Supporting Information

ABSTRACT: A new zirconocene bis(arsenide) derivative, Cp₂Zr- $(AsMes_2)_2$ (1; Cp = cyclopentadienyl, Mes = 2,4,6-trimethylphenyl), has been prepared by the metathetical reaction of 2 equiv of LiAsMes₂ with Cp₂ZrCl₂ and structurally characterized. Efforts to prepare Cp₂ZrCl(AsMes₂) (2) by reaction of 1 equiv of LiAsMes₂ with Cp2ZrCl2 yielded a mixture of products that could not be separated, including 1 and 2, as identified by ¹H NMR spectroscopy.



Compound 1 thermally decomposes with formation of As₂Mes₄, suggestive of reductive elimination to form an As-As bond. Further evidence for reductive elimination comes from effective interception of a putative zirconium(II) intermediate with diphenylacetylene to give $Cp_2Zr(C_4Ph_4)$.

he organometallic chemistry of complexes featuring metal-arsenic σ or π bonds is vastly less developed than that for phosphorus.¹ This is becoming a somewhat odd observation with the surge in interest regarding catalytic bond formation between heavier main-group elements in recent years.² An increased understanding of these bonds is of importance due to multiple mechanistic possibilities in such reactions. For example, group 4 metal complexes are known to engage in dehydrocoupling via σ -bond metathesis or α -elimination steps.^{2c,d,j,k,3} Reductive elimination is a wellknown reaction for group 4 metal complexes,⁴ but this step has not yet been implicated in catalytic dehydrocoupling reactions, despite this being a reported stoichiometric route to diphosphines and distibines.⁵

Much of what is known in zirconium and group 4 arsenido chemistry comes from Hey-Hawkins and co-workers, who prepared Cp₂Zr[As(SiMe₃)₂]₂ and Cp'₂ZrCl[As(SiMe₃)₂] (Cp' = $C_5H_5^-$, $C_5MeH_4^-$), provided structural characterization, and explored the reactivity of the Zr-As bond.⁶ The original complex in this series, Cp2Zr(AsPh2)2, was spectroscopically characterized as reported by Wade et al. in 1984.7 In the solidstate structure of Cp₂Zr[As(SiMe₃)₂]₂, inequivalent arsenic centers are observed, a feature attributed to ligand-to-metal π donation from one rather than both centers. This behavior was originally described by Baker and co-workers for related bis(phosphide) derivatives.⁸

We have investigated zirconium-arsenido chemistry using the $(N_3N)Zr$ $(N_3N = N(CH_2CH_2NSiMe_3)_3^{3-})$ platform.⁹ In those studies, we were acutely interested in the first observation of dehydrocoupling of arsenic and the related mechanistic differentiation based on primary versus secondary substitution at arsenic. Additionally, we have also observed zirconiumcatalyzed hydroarsination of terminal alkynes. This prior work in organoarsine catalysis has led to a reconsideration of the family of metallocene complexes, as particularly related to As-As bond formation.

In this report, the new complex $Cp_2Zr(AsMes_2)_2$ (1) has been prepared by the metathetical reaction of LiAsMes₂ with zirconocene dichloride. Interestingly, 1 is susceptible to a ligand-induced reductive elimination event to form As₂Mes₄, which appears to be the first example of such a transformation for arsenic.

RESULTS AND DISCUSSION

Preparation and Characterization of Complexes. Reaction of Cp2ZrCl2 with 2 equiv of LiAsMes2, generated in situ by reaction of MeLi and Mes₂AsH, afforded a dark blue solution from which analytically pure purple crystals of $Cp_2Zr(AsMes_2)_2$ (1) formed in 49% yield (eq 1). The reaction

reliably provides approximately 50% yield. However, in some instances higher isolated yields are possible. The low isolated yield appears to be a function of crystallization, as NMR spectra on crude reaction products appear to be predominately complex 1.

The NMR spectra of complex 1 are simple but highly indicative. A singlet at δ 5.53 is assigned to the cyclopentadienyl ligand, and singlet resonances at δ 2.62 and 2.16 are assigned as the methyl substituents in the ¹H NMR spectrum. Likewise, the ¹³C NMR spectrum clearly indicates cyclopentadienyl, mesityl, and methyl resonances, on the basis of the chemical shift. Infrared spectroscopic data were collected on complex 1, but these were largely uninformative. Fingerprint data are reported for confirmation.

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Crystals suitable for X-ray diffraction analysis were grown from pentane solution, and the molecular structure of **1** is shown in Figure 1. The crystal was plagued with a disordered



Figure 1. Molecular structure of $Cp_2Zr(AsMes_2)_2$ (1) with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity.

solvent molecule of crystallization. For convenience, this disordered solvent was removed from the data set using the SQUEEZE function of the PLATON software package.¹⁰ As expected, there is differential bonding between the two arsenic atoms and zirconium. Not only is Zr–As(2) approximately 0.07 Å shorter than Zr–As(1), the sum of angles at As(2) is approaching planar at approximately 355° (Table 1). This difference and the lengths of the Zr–As bonds are highly similar to those seen by Hey-Hawkins.^{6a} Interestingly, the As–C bond lengths are shorter for As(2), which is involved in greater ligand-to-metal π bonding than As(1). This is a small difference ($\Delta \approx 0.010-0.019$ Å), but it is also consistent with the trend for As–Si bonds as measured for Cp₂Zr[As-(SiMe₃)₂]₂^{6a} and may be a consequence of hybridization at arsenic.

Attempts to prepare $Cp_2ZrCl(AsMes_2)$ (2) by reaction of Cp_2ZrCl_2 with 1 equiv of in situ generated LiAsMes_2 afforded a mixture of 1 and starting zirconocene (eq 2). The ¹H NMR



spectrum of crude reaction mixtures showed resonances for starting Cp_2ZrCl_2 and 1. Additional resonances were seen, which may have corresponded to the targeted product, but this could not be isolated from 2 or more efficient conversion solicited. This is an interesting observation in light of the relative ease with which Hey-Hawkins and co-workers could prepare $Cp'_2ZrCl[As(SiMe_3)_2]$ by the same synthetic strategy.^{6a}

However, for reactions of group 4 metallocenes with phosphide anions often give the double-substitution product, despite the stoichiometry.^{1b}

Decomposition of Cp₂Zr(AsMes₂)₂ (1). Despite high air and moisture sensitivity, compound 1 exhibits good stability as a solid under nitrogen at -30 °C. However, upon extended storage as a solid at ambient temperature, some decomposition was observed. To better understand this behavior, the decomposition process was monitored spectroscopically in benzene- d_6 solution. Solution samples of 1 were stable in benzene- d_6 at ambient temperature for extended periods under nitrogen. Upon heating for hours at 90 °C, several new mesitylcontaining compounds were observed. Among these, $(Mes_2As)_2$ (3) was detected by ¹H NMR spectroscopy (eq 3).¹¹ The formation of 3 suggested that reductive elimination

$$\overbrace{\substack{z_{r}, AsMes_{2} \ \Delta \\ AsMes_{2} \ d}}^{Mes_{2}As-AsMes_{2}} \overbrace{\substack{z_{r}, AsMes_{2} \ d}}^{Mes_{2}As-AsMes_{2}}$$

may be occurring. The concomitant deposition of a precipitate during the reaction indicated that the resultant zirconocene products were unstable.

It was hypothesized that the zirconium byproduct of reductive elimination may be hampering a clean reaction. An effort to trap the putative Zr(II) complex was made to facilitate the reaction. Thus, a benzene- d_6 solution of complex 1 was heated in the presence of 5 equiv of diphenylacetylene, which resulted in complete conversion to 3 and quantitative formation of $Cp_2Zr(C_4Ph_4)$ (eq 4). Larger excesses of diphenylacetylene



prompted the reaction to proceed at a greater qualitative rate. While this is not definitive evidence of a Zr(II) intermediate during this reaction, oxidative coupling of alkynes at formally Zr(II) compounds, is a well-described transformation.¹²

The increase in qualitative rate of diarsine formation upon addition of diphenylacetylene is suggestive of a ligand-induced reductive elimination. This is a somewhat unsurprising feature of this chemistry, recalling that associative, ligand-induced reductive elimination reactions have been known for zirconocene complexes for more than 30 years.^{4b} However, As-As bond formation by reductive elimination appears to be unique in the literature.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

Zr-As(1)	2.7286(4)	As(1)–C(11)	1.973(3)
Zr-As(2)	2.6581(4)	As(1) - C(17)	1.974(3)
$Zr-Cp(1)^{a}$	2.183(3)	As(1) - C(23)	1.963(3)
$Zr-Cp(1)^{b}$	2.183(3)	As(1) - C(29)	1.956(3)
C(11)-As(1)-C(17)	104.17(12)	C(29)-As(1)-C(23)	104.76(12)
C(11)-As(1)-Zr	115.24(9)	C(29)-As(1)-Zr	118.54(9)
C(17)-As(1)-Zr	126.91(10)	C(23)-As(1)-Zr	131.64(10)

^aDistance to a centroid formed by atoms C(1)-C(5). ^bDistance to a centroid formed by atoms C(6)-C(10).

In summary, a new bis(arsenido) complex has been prepared, and its decomposition via apparent reductive elimination to form an As–As has been examined. While there have been reports that diphosphines can be formed via reductive and oxidative processes^{5a,13} and there is evidence for Sb–Sb formation by reductive elimination from a bis(stibido) complex of hafnium,^{5b} this process is, to the best of our knowledge, a unique route to As–As bonds and may represent an inroad to novel synthesis involving arsenic.

EXPERIMENTAL DETAILS

Manipulations were performed under a nitrogen with dry, oxygen-free solvents using an M. Braun glovebox. Benzene- d_6 was degassed and then dried over NaK alloy. Celite-454 was heated to a temperature greater than 180 °C under dynamic vacuum for at least 8 h. NMR spectra were recorded with a Bruker AXR 500 MHz spectrometer in benzene- d_6 and are reported with reference to residual solvent resonances (δ 7.15 and δ 128.0). Infrared spectra were collected on a Bruker Alpha FT-IR spectrometer with an ATR head. Elemental analysis was performed on an Elementar microCube instrument. Reagents were obtained from commercial suppliers and dried by conventional means. Zirconocene dichloride was purchased from Strem Chemicals, and dimesitylarsane¹⁴ was prepared by reduction of Mes₃As¹⁵ with lithium metal in THF followed by quenching with degassed water and crystallization.

Preparation of Cp₂ Zr(AsMes₂)₂ (1). A 10 mL diethyl ether solution of dimesitylarsane (304.5 mg, 0.9688 mmol) was cooled to -30 °C, and methyllithium (0.61 mL, 0.98 mmol) was added slowly. The resulting yellow solution was warmed to ambient temperature and stirred for 1 h, and then it was cooled to -30 °C. Zirconocene dichloride (141.6 mg, 0.484 mmol) was suspended in 10 mL of diethyl ether and cooled to -30 °C. The cold Mes₂AsLi solution was added dropwise to the cold suspension of Cp_2ZrCl_2 , resulting in a dark blue solution. The solution was filtered through Celite after 1 h of stirring at ambient temperature. Solvent was removed under reduced pressure until a solid appeared, and then the solution was warmed to ambient temperature to redissolve the solids. The solution was filtered then cooled to $-30\ ^\circ C$ for several days, yielding 1 as purple crystals in two crops (201 mg, 0.273 mmol, 49%). ¹H NMR (500 MHz): δ 6.87 (s, 8 H, CH), 5.53 (s, 10 H, C₅H₅), 2.62 (s, 24 H, CH₃), 2.16 (s, 12 H, CH₃). ¹³C{¹H} NMR (125.8 MHz): δ 144.4 (s, C₆H₂Me₃), 136.8 (s, $C_6H_2Me_3$, 129.2 (s, $C_6H_2Me_3$), 128.3 (s, $C_6H_2Me_3$), 105.8 (s, Cp), 25.7 (s, CH₃), 20.9 (s, CH₃). IR: 2953 w, 2910 w, 1597 w, 1430 m, 1365 m, 1291 w, 1011 m, 848 m, 803 s, 550 m cm⁻¹. Anal. Calcd for C46H54As2Zr: C, 65.15; H, 6.42. Found: C, 65.08; H, 6.49.

Attempted Preparation of Cp₂ZrCl(AsMes₂) (2). A 7 mL diethyl ether solution of dimesitylarsane (152.2 mg, 0.4844 mmol) was cooled to -30 °C, and methyllithium (0.30 mL, 0.49 mmol) was added slowly. The resulting yellow solution was warmed to ambient temperature and stirred for 1 h, and then it was cooled to -30 °C. Zirconocene dichloride (141.6 mg, 0.484 mmol) was suspended in 5 mL of diethyl ether and cooled to -30 °C. The cold Mes₂AsLi solution was added dropwise to the cold suspension of Cp₂ZrCl₂, resulting in a purple solution. The solution was reacted and worked up as above to yield a light purple powder, which was found to be an impure mixture of 1 and Cp₂ZrCl₂ by NMR spectroscopy.

Reaction of 1 with Diphenylacetylene. A J. Young NMR tube was charged with a 1 mL benzene- d_6 solution of 1 (12.0 mg, 1.41 × 10^{-2} mmol) and diphenylacetylene (12.6 mg, 7.05 × 10^{-2} mmol). The tube was sealed and an initial ¹H NMR spectrum collected. The dark purple solution was then placed in a 100 °C oil bath for 2 h, resulting in an orange solution. A final ¹H NMR experiment was run, confirming complete conversion to 3 and Cp₂Zr(C₄Ph₄).

X-ray Crystallography. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo K α , λ = 0.71073 Å) at 125 K. A suitable crystal of 1 was mounted in a nylon loop with Paratone-N cryoprotectant oil. The structure was solved using direct methods and standard difference map techniques and was refined by

full-matrix least-squares procedures on F^2 with SHELXTL (version 6.14).¹⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. A disordered solvent molecule (ether or pentane) was included in the unit cell but could not be satisfactorily modeled. Therefore, that solvent was treated as a diffuse contribution to the overall scatting without using specific atom positions by the SQUEEZE function in the PLATON program.¹⁰ SQUEEZE output data (.lis file) are included as Supporting Information. Crystal data and structure refinement parameters are given in Table 2.

Tab	le 2.	Crystal	Data and	d Structure	Refinement	Parameters
for	Com	plex 1				

formula ^a	C56H66As2Zr
M_r^a	980.15
cryst syst	orthorhombic
color	purple
a/Å	20.9687(18)
b/Å	22.0733(19)
c/Å	9.3097(8)
$\alpha = \beta = \gamma/\deg$	90
unit cell V/Å ³	4309.0(6)
space group	Pnn2
Z	4
heta range/deg	1.34-25.04
μ/mm^{-1}	1.819
N	40 600
$N_{\rm ind}$	7616
R _{int}	0.0314
Flack x	0.014(6)
$\mathrm{R1}^{a}(I > 2\sigma(I))$	0.0279
$wR2^{b} (I > 2\sigma(I))$	0.0639
$\Delta ho_{ m max}$ /e Å ⁻³	0.486
$\Delta ho_{ m min}/ m e~ \AA^{-3}$	-0.356
GOF on R1	1.042

^{*a*}Calculated with complete cell contents prior to SQUEEZE operation. ^{*b*}R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. [*c*] wR2 = { $\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]$ }^{1/2}.

ASSOCIATED CONTENT

S Supporting Information

A table, a figure, and a CIF file giving crystallographic data, a SQUEEZE output file for 1, and an NMR spectrum of the reaction of 1 with diphenylacetylene (pfd). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 873948 (1) has been deposited at the Cambridge Crystallographic Data Centre.

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Notes

The authors declare no competing financial interest.

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Organometallics

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