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# Synthesis and Structural Characterization of Novel Rhodium−Diacylarsenido Complexes

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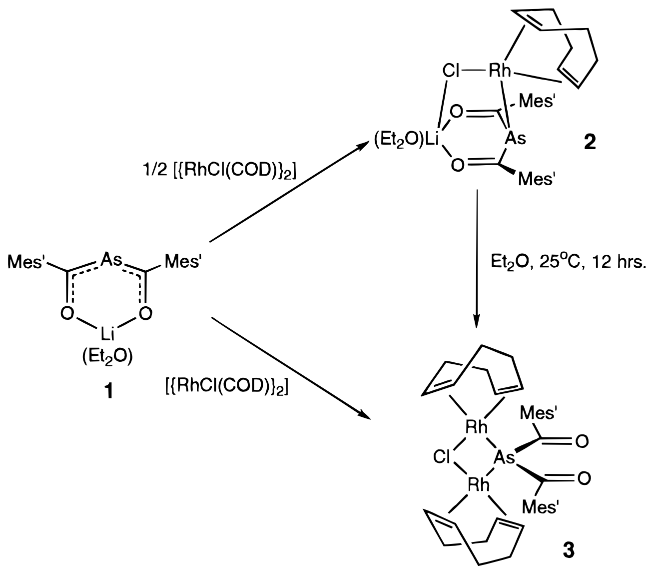
*Summary: The reaction of* [Li{$\eta^2$-OC(Mes′)AsC(Mes′)O}(OEt$_2$)], *Mes′* = $C_6H_2Pr^i{}_3$-2,4,6, *with* [{RhCl(COD)}$_2$], *COD* = 1,5-$C_8H_{12}$, *in either a 1:1 or 2:1 stoichiometry yields the novel rhodium−diacylarsenido complexes,* [{Rh(COD)}$_2$-$\mu$-Cl-$\mu$-{As[C(O)Mes′]$_2$}] *and* [Rh(COD){$\eta^1$-As[C(Mes′)O]$_2$Li(OEt$_2$)Cl}], *respectively. The X-ray crystal structure of each is described and mechanisms for their formations proposed.*

## Introduction

$\beta$-Diketonates are one of the most versatile and extensively studied ligand systems in inorganic chemistry.[1] Their complexes with transition metals exhibit a wide range of coordination modes but O,O-chelation is by far the most common. Such complexes have numerous applications in areas ranging from organic synthesis to chemical vapor deposition processes.[1,2] In our laboratory we are interested in investigating the analogy between the heavier group 15 elements and the valence isoelectronic CR (R = alkyl, H) fragment. To this end we have recently reported the first crystallographically characterized 2-stiba- and 2-arsa-1,3-dionatolithium complexes, [{[Li{$\eta^2$-OC(Bu$^t$)EC(Bu$^t$)O}(DME)$_{0.5}$]$_2$}$_\infty$], E = Sb or As, which are structurally similar to their $\beta$-diketonato counterparts.[3] Prior to this report several main-group[4] and transition-metal[5] complexes of related 2-phospha-1,3-dionate ligands had been described in which the ligand can coordinate the metal in either an $\eta^2$-O,O- or $\eta^1$-P-fashion. In addition, several transition-metal−diacylarsenido complexes have been reported[6] though, to the best of our knowledge, none have been structurally characterized. We have begun to examine the use of 2-arsa-1,3-dionatolithium species, e.g. **1**, as transfer reagents in the synthesis of a similar range of compounds which include the first structurally authenticated transition-metal−diacylarsenido complexes reported herein.

**Scheme 1**



## Results and Discussion

In an attempt to form the monomeric arsadionato−rhodium complex, [Rh(COD){OC(Mes′)AsC(Mes′)O}], a diethyl ether suspension of [{RhCl(COD)}$_2$] was treated with 2 equiv of **1**. Remarkably, this led to an almost quantitative yield of **2** (Scheme 1) which can be considered as an intermediate in the intended salt elimination reaction. Compound **2** is not thermally stable in the solid

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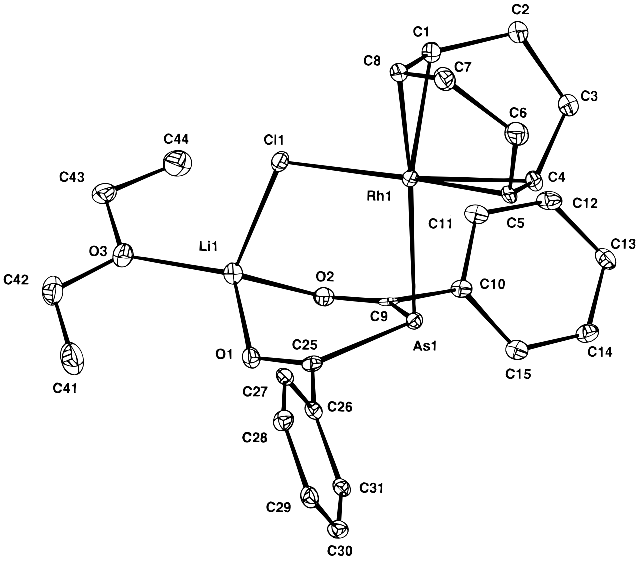

**Figure 1.** Molecular structure of **2** (isopropyl groups omitted for sake of clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−As(1) 2.5206(7), As(1)−C(25) 1.991(5), As(1)−C(9) 1.991(5), Cl(1)−Li(1) 2.390(9), O(1)−C(25) 1.226(6), O(1)−Li(1) 1.922(10), O(2)−C(9) 1.221(6), O(2)−Li(1) 1.965(10), O(3)−Li(1) 1.963(10), Cl(1)−Rh(1)−As(1) 93.30(4), C(25)−As(1)−C(9) 98.3(2), C(25)−As(1)−Rh(1) 104.70(14), C(9)−As(1)−Rh(1) 95.21(13), Rh(1)−Cl(1)−Li(1) 112.3(2), C(25)−O(1)−Li(1) 121.8(3), C(9)−O(2)−Li(1) 120.3(4), O(2)−C(9)−As(1) 127.1(4), O(1)−Li(1)−O(2) 95.4(4), O(1)−Li(1)−Cl(1) 103.0(4), O(2)−Li(1)−Cl(1) 100.1(4).

state and decomposes to intractable products over ca. 7 days at room temperature. By contrast, ethereal solutions of **2** decompose over 12 h at 25 °C to yield lithium chloride and the dinuclear rhodium complex, **3** (27%), as the only identifiable products; presumably via some form of redistribution reaction. A direct synthesis to this compound was devised whereby [{RhCl(COD)}$_2$] was treated with only 1 equiv of **1** which afforded **3** in a 76% yield after recrystallization from diethyl ether. In this case the reaction was complete in less than 1 h and most likely occurs via an initial formation of **2** from which LiCl is rapidly displaced by the RhCl(COD) fragment.

The $^1$H and $^{13}$C NMR spectroscopic data for compounds **2** and **3** support their proposed structures. Additionally, the FAB mass spectrum of **3** displays a cluster of peaks corresponding to its molecular ion. In contrast, no molecular ion was seen in the mass spectrum of **2**, but a cluster with the correct isotopic distribution pattern for the loss of the coordinated diethyl ether from this molecule was observed.

The molecular structures of **2** and **3** are depicted in Figures 1 and 2, respectively (see also Table 1). In both, the Rh centers have slightly distorted square planar coordination geometries. Their As−C distances all lie close to the normal value for single bonds (1.96 Å),[7] while their C−O bond lengths are in good agreement with the typical double-bonded distance (1.19 Å).[7] Therefore, in **2** and **3** the hetero-ligand can be viewed as a localized diacylarsenide rather than a delocalized arsadionate, as is the case in **1**. In accordance with this description is the distorted pyramidal geometry (Σ angles = 298.2°) for As(1) in **2** and a near tetrahedral geometry for the arsenic center in **3**. This suggests that the sp$^3$-hybridized As(1) center in **2** has a stereochemically active lone pair and consequently that the molecule is best described as a rhodium(I)−diacylarsenido complex, [Rh(COD){$\eta^1$-As[C(O)Bu$^t$]$_2$}], that forms an adduct with a solvated lithium chloride molecule via lone pair donation from both O centers to the tetrahedral Li(1) center, and a similar donation from Cl(1) to Rh(1). All of the bond lengths incorporating these centers are in the normal range. The six-membered chelate ring in **2** is nonplanar since the As and Li centers both lie significantly above the least-squares plane defined by O(1), O(2), C(9), and C(25), [As(1) 0.924(11) Å, Li(1) 0.314(7) Å]. In a fashion similar to **2**, complex **3** can be seen as an adduct of [Rh(COD){$\eta^1$-As[C(O)Bu$^t$]$_2$}] with a RhCl(COD) fragment, though in this case a crystallographic 2-fold axis prevents any distinction being made between the two rhodium centers.

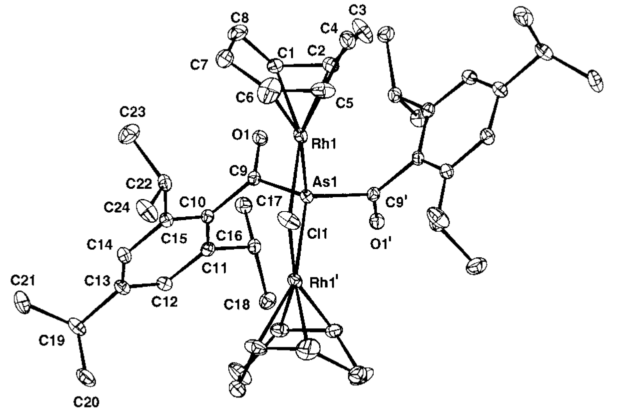

**Figure 2.** Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Rh(1)−Cl(1) 2.4220(8), Rh(1)−As(1) 2.4321(4), As(1)−C(9) 2.019(3), O(1)−C(9) 1.201(4), Cl(1)−Rh(1)−As(1) 80.80(3), C(9)−As(1)−C(9)′ 97.9(2), C(9)−As(1)−Rh(1) 112.79(8), C(9)′−As(1)−Rh(1) 117.79(8), Rh(1)−As(1)−Rh(1)′ 98.92(2), Rh(1)−Cl(1)−Rh(1)′ 99.48(4), O(1)−C(9)−As(1) 119.9(2).

**Table 1. Crystal Data for Compounds 2 and 3**

| | **2** | **3** |
|---|---|---|
| chemical formula | $C_{44}H_{68}O_3LiClAsRh$ | $C_{48}H_{70}O_2ClAsRh_2$ |
| fw | 865.20 | 995.23 |
| cryst syst | orthorhombic | monoclinic |
| space group | *Pcab* | *C*2/*c* |
| $a$ (Å) | 17.3477(6) | 17.3253(9) |
| $b$ (Å) | 19.1711(8) | 10.7319(4) |
| $c$ (Å) | 26.3489(9) | 24.8474(11) |
| $\beta$ (deg) | 90 | 98.6310(10) |
| $V$ (Å$^3$) | 8763.0(6) | 4567.6(4) |
| $Z$ | 8 | 4 |
| $T$ (K) | 100(2) | 100(2) |
| $\lambda$ (Å) | 0.71070 | 0.71070 |
| $\rho_{calcd}$ (g cm$^{-1}$) | 1.312 | 1.447 |
| $\mu$ (Mo Kα) (cm$^{-1}$) | 12.36 | 15.36 |
| $F$ (000) | 3632 | 2056 |
| reflns collected | 62 680 | 17 833 |
| no. unique reflns | 7600 | 4476 |
| cryst size (mm) | 0.2 × 0.1 × 0.1 | 0.5 × 0.5 × 0.5 |
| $\theta$ range (deg) | 3.46−25.00 | 3.48−26.00 |
| $R^a$ (all data) | 0.1003 | 0.0434 |
| $R^a$ ($I > 2\sigma$(I)) | 0.0685 | 0.0367 |
| w$R'^{\,b}$ (all data) | 0.1550 | 0.1145 |
| w$R'^{\,b}$ ($I > 2\sigma(I)$) | 0.1044 | 0.0952 |

$^a$ $R = \Sigma(\Delta F)/\Sigma(F_o)$. $^b$ w$R' = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.000$ for **2** and 0.033 for **3**.

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## Conclusion

In summary, we have described the synthesis and structural characterization of two novel diacylarsenido−rhodium complexes. Remarkably, one of these, **2**, represents a trapped intermediate in the salt elimination reaction that forms the other, **3**. Work continues in our laboratory on a comparison of the coordination chemistry of 2-arsa- and 2-stibadionates with that of their $\beta$-diketonate counterparts.

## Experimental Section

**General Procedures.** All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or dinitrogen. The solvents diethyl ether and hexane were distilled over Na/K alloy and then freeze/thaw-degassed prior to use. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM 400 spectrometer in $C_6D_6$ and were referenced to the residual $^1$H resonances of the solvent ($^1$H NMR) or the $^{13}$C resonance of the deuterated solvent ($^{13}$C NMR), respectively. Mass spectra were recorded using a VG-autospec/Cs$^+$ ions/25kV/NBA matrix (FAB) instrument and conditions. The microanalysis of **3** was obtained from the University of Wales, Cardiff Microanalytical Service. A reproducible microanalysis of **2** could not be obtained because of its thermal instability at room temperature. Melting points were determined in sealed glass capillaries under argon and are uncorrected. The starting materials, [Li{$\eta^2$-OC(Mes′)AsC(Mes′)O}(OEt$_2$)][3] and [{RhCl(COD)}$_2$],[8] were prepared by published procedures.

**Synthesis of 2.** A solution of **1** (0.27 g, 0.44 mmol) in 10 mL of $Et_2O$ was added to a suspension of [{RhCl(COD)}$_2$] (0.11 g, 0.22 mmol) in 10 mL of $Et_2O$ at −78 °C. The suspension was slowly warmed to 0 °C and stirred for 30 min to yield an orange solution. This was concentrated in vacuo to ca. 3 mL and slowly cooled to −30 °C to yield **2** as pale orange rods (0.376 g, 98%): mp 88−90 °C (dec); $^1$H NMR (400 MHz, $C_6D_6$, 298 K) $\delta$ 1.09 (d, 24H, $^3J_{HH} = 6.1$ Hz, *o*-CH(C*H*$_3$)$_2$, 1.10 (d, 12H, $^3J_{HH} = 7.1$ Hz, *p*-CH(C*H*$_3$)$_2$), 1.05 (t, 6H, $^3J_{HH} = 7.4$ Hz, OCH$_2$C*H*$_3$), 1.37 (br, 4H, COD CH$_2$), 1.63 (br, 4H, COD CH$_2$), 2.03 (septet, 4H, $^3J_{HH} = 6.1$ Hz, *o*-C*H*(CH$_3$)$_2$), 2.67 (septet, 2H, $^3J_{HH} = 7.1$ Hz, *p*-C*H*(CH$_3$)$_2$), 3.28 (br, 2H, COD CH), 3.60 (q, 4H, $^3J_{HH} = 7.4$ Hz, OC*H*$_2$CH$_3$), 3.78 (br, 2H, COD CH), 7.14 (s, 4H, aromatic CH); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 298 K) $\delta$ 15.3 (OCH$_2$*C*H$_3$), 24.2 (*o*-CH(*C*H$_3$)$_2$), 24.3 (*p*-CH(*C*H$_3$)$_2$), 25.3 (*o*-*C*H(CH$_3$)$_2$), 29.5 (COD CH$_2$), 30.8 (*p*-*C*H(CH$_3$)$_2$), 33.1 (COD CH$_2$), 66.0 (O*C*H$_2$CH$_3$), 70.9 (d, $^1J_{RhC} = 14.02$ Hz, COD CH), 90.3 (d, $^1J_{RhC} = 10.2$ Hz, COD CH), 121.3 (aromatic CH), 143.9, 145.1, 149.9 (aromatic quaternary), 239.6 (AsCO); FAB mass spectrum (NBA matrix) *m/z* 791 (M$^+$ − Et$_2$O, 25%), 682 (M$^+$ − (Et$_2$O + COD), 10%), 587 (M$^+$ − (Et$_2$O + 2,4,6-Pr$^i{}_3$Ph), 100%); IR (Nujol, cm$^{-1}$) 1625(m), 1605(s).

**Synthesis of 3.** A solution of **1** (0.39 g, 0.63 mmol) in 10 mL of $Et_2O$ was added to a suspension of [{RhCl(COD)}$_2$] (0.31 g, 0.62 mmol) in 20 mL of $Et_2O$ at −78 °C. The suspension was slowly warmed to room temperature and stirred for 1 h. Volatiles were removed in vacuo, and the residue was extracted with hexane (30 mL) and filtered. The hexane was removed in vacuo, and the residue was recrystallized from $Et_2O$ (5 mL) to yield orange blocks of **3** (0.475 g, 75.8%): mp 119−121 °C (dec); $^1$H NMR (400 MHz, $C_6D_6$, 298 K) $\delta$ 1.32 (d, 12H, $^3J_{HH} = 6.5$ Hz, *p*-CH(C*H*$_3$)$_2$), 1.44 (br, 12H, *o*-CH(C*H*$_3$)$_2$), 1.62 (br, 8H, COD CH$_2$), 1.74 (br, 8H, COD CH$_2$), 1.83 (br, 12H, *o*-CH(C*H*$_3$)$_2$), 2.24 (br, 4H, COD CH), 2.33 (br, 4H, COD CH), 2.89 (septet, 2H, $^3J_{HH} = 6.5$ Hz, *p*-C*H*(CH$_3$)$_2$), 3.78 (br, 4H, *o*-C*H*(CH$_3$)$_2$, 7.23 (s, 4H, aromatic CH); $^{13}$C NMR (100.6 MHz, $C_6D_6$, 298 K) $\delta$ 23.2 (*p*-*C*H(CH$_3$)$_2$), 24.2 (*p*-CH(*C*H$_3$)$_2$), 26.4 (*o*-*C*H(CH$_3$)$_2$), 29.5 (br, COD CH$_2$), 31.2 (*o*-CH(*C*H$_3$)$_2$), 33.2 (br, COD CH$_2$), 34.8 (*o*-CH(*C*H$_3$)$_2$), 71.3 (br, COD CH), 90.9 (br, COD CH), 120.9 (aromatic CH), 142.3, 143.9, 148.9 (aromatic quaternary), 223.9 (AsCO); FAB mass spectrum (NBA matrix) *m/z* 994 (M$^+$, 5%), 886 (M$^+$ − COD, 40%), 778 (M$^+$ − 2COD, 10%), 763 (M$^+$ − CO(2,4,6-Pr$^i{}_3$Ph), 100%); IR (Nujol, cm$^{-1}$) 1667(s), 1651(s). Calcd for $C_{48}H_{70}O_2AsClRh_2$: C, 57.92; H, 7.09. Found: C, 58.22; H, 6.89.

**X-ray Structure Determinations of 2 and 3.** Crystals of both compounds were mounted on a glass fiber using silicone grease and cooled on the diffractometer. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation using $\phi$ rotations with 2° frames and a detector-to-crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN.[9] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack.[9] Structures were solved using the direct methods option of SHELXS-97[10] and developed using conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97).[10] In general, all non-hydrogen atoms were refined anisotropically, while hydrogen atoms were fixed in idealized positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. Some disorder was noted for the COD ligand in **3** which was modeled in terms of two positions each for C(4) and C(7), both of 50% occupancy. All calculations were carried out on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer. Crystal data and details of the data collections and refinements are given in Table 1.

**Acknowledgment.** We thank the Leverhume Trust for funding (for S.J.B.) and King's College London and the EPSRC for provision of the diffractometer system.

**Supporting Information Available:** Tables of crystal data, positional and thermal parameters, and bond angles and distances for **2** and **3** (23 pages). Ordering information is given on any current masthead page.

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