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ELECTRONIC SUPPORTING INFORMATION FOR

A Surprise Landing on the *Terra Incognita* of Macrocyclic Dibridgehead Diorganoarsines: Syntheses, Structures, and Reactivities

Samuel R. Zarcone, Peter J. Verardi, Nattamai Bhuvanesh, and John A. Gladysz*

[a]Department of Chemistry, Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA E-mail: gladysz@mail.chem.tamu.edu

Experimental Section

General. Reactions were conducted under nitrogen atmospheres unless otherwise noted. Materials were utilized as follows: CH_2Cl_2, THF, hexanes, and toluene, purified by a Glass Contour system; EtOAc and MeOH (2 × ≥99.5%, Sigma Aldrich), $CDCl_3$ (Cambridge Isotopes), $Bu_4N^+\ Cl^-$ (≥97%, Sigma Aldrich), H_2O_2 (35 wt%, BDH), $Me_2S{\cdot}BH_3$ (2.0 M in THF, Sigma Aldrich), $PtCl_2$ (98%, Ambeed), $NiCl_2(DME)$ (98%, Ambeed), $[Rh(Cl)(COD)]_2$ (42% Rh, Pressure Chemicals), silica gel (40-63 µm mesh, Silicycle), and neutral alumina (Brockmann I, for chromatography, 40-300 µm mesh, 60A, Acros), used as received. Molecular sieves (3Å, Beantown Chemical) were activated by heating in vacuum (120 °C, 12 h).

NMR spectra were recorded on standard FT spectrometers at ambient probe temperatures and referenced as follows (δ, ppm): ^1H: residual internal $CHCl_3$ (7.26); $^{13}C\{^1H\}$: internal $CDCl_3$ (77.16). Melting points were determined on a Stanford Research Systems (SRS) MPA100 (OptiMelt) automated device. Microanalyses were conducted by Atlantic Microlab. Atmospheric pressure chemical ionization mass spectroscopy (APCI-MS) was carried out with a Thermo Scientific Q Exactive Focus instrument.

$As((CH_2)_{10})_3As$ (1a). A flame dried Schlenk flask was charged with *trans*-$[Fe(CO)_2(NO)(As((CH_2)_{10})_3As)]^+\ BF_4^-$ (**3a**; 0.158 g, 0.198 mmol), $Bu_4N^+\ Cl^-$ (0.165 g, 0.594 mmol), and CH_2Cl_2 (15 mL) with stirring, and fitted with a reflux condenser. The solution was refluxed (3 d), and the solvent removed from the dark green solution by oil pump vacuum. The sample was dissolved in 1:1 v/v hexanes/CH_2Cl_2 and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was washed with 1:1 v/v hexanes/CH_2Cl_2. The solvent was removed from the eluate by oil pump vacuum. The residue was rinsed with MeOH and EtOAc, collected by filtration, and dried by oil pump vacuum to give **1a** as a white crystalline solid (0.038 g, 0.067 mmol, 34%), mp 112-114 °C (open capillary). Anal. Calcd. for $C_{30}H_{60}As_2$ (570.64): C, 63.14; H, 10.50. Found: C, 63.15; H, 10.61.

NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 1.50-1.43 (br m, 6H), 1.41-1.28 (m, 24H); $^{13}C\{^1H\}$ (125 MHz) 31.01 (s, CH_2), 27.81 (s, CH_2), 26.88 (s, CH_2), 25.29 (s, CH_2), 23.27 (s, CH_2).

As((CH$_2$)$_{12}$)$_3$As (1b). A flame dried Schlenk flask was charged with *trans*-[Fe(CO)$_2$(NO)-(As((CH$_2$)$_{12}$)$_3$As)]$^+$ BF$_4^-$ (**3b**; 0.050 g, 0.056 mmol), Bu$_4$N$^+$ Cl$^-$ (0.023 g, 0.085 mmol), and CH$_2$Cl$_2$ (8 mL) with stirring. After 14 h, the solvent was removed from the dark green solution by oil pump vacuum. The sample was dissolved in 1:1 v/v hexanes/CH$_2$Cl$_2$ and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was washed with 1:1 v/v hexanes/CH$_2$Cl$_2$. The solvent was removed from the eluate by oil pump vacuum to give **1b** as a white crystalline solid (0.028 g, 0.043 mmol, 77%), mp 54-56 °C (open capillary). Anal. Calcd. for C$_{36}$H$_{72}$As$_2$ (654.80): C, 66.03; H, 11.08. Found: C, 65.94; H, 11.10.

NMR (CDCl$_3$, δ in ppm): ^{1}H (500 MHz) 1.51-1.44 (br m, 16H), 1.41-1.27 (m, 56H); ^{13}C {^{1}H} (125 MHz) 31.42 (s, CH$_2$), 29.86 (s, CH$_2$), 28.62 (s, CH$_2$), 28.55 (s, CH$_2$), 28.19 (s, CH$_2$), 26.21 (s, CH$_2$).

As((CH$_2$)$_{14}$)$_3$As (1c). A flame dried Schlenk flask was charged with *trans*-[Fe(CO)$_2$(NO)-(As((CH$_2$)$_{14}$)$_3$As)]$^+$ BF$_4^-$ (**3c**; 0.170 g, 0.175 mmol), Bu$_4$N$^+$ Cl$^-$ (0.073 g, 0.26 mmol), and CH$_2$Cl$_2$ (26 mL) with stirring. After 14 h, the solvent was removed from the dark green solution by oil pump vacuum. The sample was dissolved in 1:1 v/v hexanes/CH$_2$Cl$_2$ and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was washed with 1:1 v/v hexanes/CH$_2$Cl$_2$. The solvent was removed from the eluate by oil pump vacuum to give **1c** as a white crystalline solid (0.097 g, 0.131 mmol, 75%), mp 62-64 °C (open capillary). Anal. Calcd. for C$_{42}$H$_{84}$As$_2$ (738.96): C, 68.26; H, 11.46. Found: C, 68.08; H, 11.43.

NMR (CDCl$_3$, δ in ppm): ^{1}H (500 MHz) 1.52-1.41 (br m, 16H), 1.40-1.23 (m, 68H); ^{13}C {^{1}H} (125 MHz) 31.77 (s, CH$_2$), 29.87 (s, CH$_2$), 29.38 (s, CH$_2$), 29.30 (s, CH$_2$), 28.82 (s, CH$_2$), 26.51 (s, CH$_2$), 24.51 (s, CH$_2$). HRMS (APCI, *m/z*): calcd for C$_{42}$H$_{84}$As$_2$ [M + H]$^+$, 739.5078. Found, 739.5116.

As((CH$_2$)$_{12}$)$_3$As·2BH$_3$ (1b·2BH$_3$). A flame dried Schlenk flask was charged with **1b** (0.142 g, 0.217 mmol), Me$_2$S·BH$_3$ (2.0 M in THF; 0.73 mL, 1.457 mmol), and THF (4 mL) with stirring. After 3 d, the solvent was removed from the clear solution by oil pump vacuum. The sample was dissolved in hexanes and applied to a bed of silica gel (2.5 × 5.0 cm), which was washed with hexanes and then CH_2Cl_2. The solvent was removed from the eluate by oil pump vacuum to give **1b**·$2BH_3$ as a clear oil (0.139 g, 0.204 mmol, 94%). Anal. Calcd. for $C_{36}H_{78}As_2B_2$ (682.47): C, 63.36; H, 11.52. Found: C, 63.42; H, 11.41.

NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 1.68-1.61 (br m, 12H), 1.57-1.47 (m, 12H), 1.42-1.35 (br m, 12H), 1.34-1.26 (br m, 36H), 0.88-1.56 (br s, 6H, BH_3); $^{13}C\{^1H\}$ (125 MHz) 30.66 (s, CH_2), 28.88 (s, CH_2), 28.59 (s, CH_2), 28.07 (s, CH_2), 23.32 (s, CH_2), 21.17 (s, CH_2).

O=As((CH_2)$_{14}$)$_3$As=O (1a·2O). A vial was charged with **1a** (0.083 g, 0.112 mmol) and CH_2Cl_2 (2 mL). Then H_2O_2 (35 wt%, 2.0 mL, 20.58 mmol) was slowly added with stirring. After 14 h, methanol and CH_2Cl_2 were added and the solvent was removed in vacuo. Then 3Å molecular sieves and toluene (20 mL) was added. The sample was stirred (14 h) and filtered. The filter pad was rinsed with toluene and CH_2Cl_2. The solvent was removed from the filtrate in vacuo and the residue triturated with hexanes. The sample was dried in vacuo to give **1a**·2O[s1] as a white solid. (0.073 g, 0.095 mmol, 85%), mp 88-90 °C (open capillary). Anal. Calcd. for $C_{42}H_{84}As_2O_2\cdot(H_2O)_4$[s1] (842.03): C, 59.84; H, 11.00. Found: C, 60.13; H, 10.71.

NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 1.91-1.79 (br m, 12H), 1.63-1.49 (12H, br m), 1.40-1.29 (12H, br m), 1.27-1.15 (br m, 48H); $^{13}C\{^1H\}$ (125 MHz)[s2] 30.83 (s, CH_2), 30.70 (s, CH_2), 29.22 (br s, CH_2), 29.01 (s, CH_2), 28.90 (s, CH_2), 28.78 (s, CH_2), 28.70 (s, CH_2), 28.54 (s, CH_2), 28.42 (s, CH_2), 22.33 (s, CH_2), 22.24 (s, CH_2). IR (powder film, cm^{-1}): 2914 (s), 2849 (s), 1742 (w), 1462 (m), 1373 (w), 1261 (w), 1175 (w), 1097 (m), 1022 (w), 881 (s, $\nu_{As=O}$),[s3] 808 (m), 717 (m), 667 (w). HRMS (APCI, *m/z*): calcd for $C_{42}H_{84}As_2O_2$ $[M + H]^+$, 771.4976. Found, 771.4952.

***trans*-$\overline{\mathrm{Pt(Cl)_2(As((CH_2)_{14})_3As}}$) (4c).** A flame dried Schlenk flask was charged with **1c** (0.100 g, 0.135 mmol), $PtCl_2$ (0.044 g, 0.169 mmol), and toluene (8 mL) with stirring. After 18 h, the solvent was removed by oil pump vacuum. The residue was dissolved in 1:1 v/v hexanes/CH_2Cl_2 and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was eluted with 1:1 v/v hexanes/CH_2Cl_2. The solvent was removed from the eluate by oil pump vacuum to give a yellow oil, to which 1:1 v/v EtOAc/MeOH was added. The solvents were removed by oil pump vacuum to give **4c** a pale yellow solid (0.117 g, 0.116 mmol, 86%), mp 117-119 °C (open capillary). Anal. Calcd. for $C_{42}H_{84}As_2Cl_2Pt$ (1104.95): C, 50.20; H, 8.43. Found: C, 50.69; H, 8.69.

NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 1.89-1.83 (br m, 12H), 1.78-1.70 (m, 12H), 1.48-1.42 (br m, 12H), 1.37-1.29 (br m, 48H); $^{13}C\{^1H\}$ (125 MHz)[s4] 30.74 (s, $AsCH_2CH_2\mathit{CH}_2$), 28.24 (s, A*sCH*$_2$), 27.54 (s, CH_2), 27.44 (s, CH_2), 27.37 (s, CH_2), 24.58 (s, CH_2), 21.26 (s, $AsCH_2\mathit{CH}_2$).

***trans*-Ni(Cl)$_2$(As((CH$_2$)$_{14}$)$_3$As) (5c) A.** A flame dried Schlenk flask was charged with **1c** (0.033 g, 0.045 mmol), $NiCl_2(NCCH_3)$ (0.012 g, 0.056 mmol),[s5] and THF (5 mL) with stirring. After 18 h, the solvent was removed by oil pump vacuum. Then CH_2Cl_2 was added and the sample filtered through a glass frit. The solvent was removed from the filtrate by oil pump vacuum and the residue triturated with EtOAc. The sample was dried by oil pump vacuum to give **5c** as a purple solid (0.031 g, 0.036 mmol, 80%). **B.** A flame dried Schlenk flask was charged with **1c** (0.100 g, 0.135 mmol), $NiCl_2(DME)$ (0.037g, 0.169 mmol), and THF (15 mL) with stirring. After 18 h, the solvent was removed by oil pump vacuum. Then CH_2Cl_2 was added and the sample filtered through a glass frit. The solvent was removed from the filtrate by oil pump vacuum, and the solid rinsed with EtOAc into a filter frit. The filter cake was eluted with CH_2Cl_2, and the CH_2Cl_2 removed by oil pump vacuum to give **5c** as a purple solid (0.080 g, 0.092 mmol, 68%) dec. pt. 206 °C (open capillary). Anal. Calcd. for $C_{42}H_{84}As_2Cl_2Ni$ (868.56): C, 58.08; H, 9.75. Found: C, 58.33; H, 9.90.

NMR ($CDCl_3$, δ in ppm): ^1H (500 MHz) 1.95-1.81 (br m, 12H), 1.76-1.66 (br m, 12H), 1.56-1.47 (br m, 12H), 1.43-1.22 (br m, 48H); $^{13}C\{^1H\}$ (125 MHz)[s4] 31.10 (s, $AsCH_2CH_2\mathit{CH}_2$), 28.19 (s, $As\mathit{CH}_2$), 27.63 (s, CH_2), 27.39 (s, CH_2), 25.14 (s, CH_2), 22.07 (s, $AsCH_2\mathit{CH}_2$).

***trans*-Rh(CO)(Cl)(As((CH$_2$)$_{14}$)$_3$As) (6c).** A flame dried Schlenk flask was charged with **1c** (0.147 g, 0.199 mmol), $[Rh(Cl)(COD)]_2$ (0.059 g, 0.119 mmol), and 1:1 v/v hexanes/CH_2Cl_2 (30 mL). Then CO was aspirated through the solution. The sample was stirred under a closed CO atmosphere (18 h), and the solvent was removed by oil pump vacuum. The residue was dissolved in 1:1 v/v hexanes/CH_2Cl_2 and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was washed with 1:1 v/v hexanes/CH_2Cl_2. The solvent was removed from the eluate by oil pump vacuum. The residue was triturated several times with EtOAc and dried in vacuo to yield **6c** as a pale yellow solid (0.155 g, 0.171 mmol, 86%) dec. pt. at 146 °C (open capillary). Anal. Calcd. for $C_{43}H_{84}As_2ClORh$ (905.33): C, 57.05; H, 9.35. Found: C, 56.98; H, 9.44.

NMR ($CDCl_3$, δ /ppm): ^1H (500 MHz) 1.91-1.81 (br m, 12H), 1.72-1.63 (m, 12H), 1.45-1.39 (br m, 12H), 1.35-1.27 (br m, 48H); $^{13}C\{^1H\}$ (125 MHz)[s4] 186.9 (s, CO), 31.0 (s, $AsCH_2CH_2\mathit{C}H_2$), 28.1 (s, $As\mathit{C}H_2$), 27.9 (s, CH_2), 27.5 (s, CH_2), 27.4 (s, CH_2), 25.6 (s, CH_2), 24.9 (s, $AsCH_2\mathit{C}H_2$). IR (powder film, cm^{-1}): 2918 (w), 2849 (w), 1942 (s, $\nu_{C\equiv O}$), 1457 (m), 1260 (w), 1093 (w), 1017 (m), 801 (m), 719 (m).

***trans*-$\overline{\mathrm{Fe(CO)_3(As((CH_2)_{14})_3As}}$) (2c).** A flame dried Schlenk flask was charged with **1c** (0.029 g, 0.039 mmol), (BDA)$Fe(CO)_3$ (0.014 g, 0.049 mmol),[s6] and THF (5 mL) with stirring. After 18 h, the solvent was removed by oil pump vacuum. The sample was dissolved in 2:1 v/v hexanes/CH_2Cl_2 and applied to a bed of neutral alumina (2.5 × 5.0 cm), which was washed with 2:1 v/v hexanes/CH_2Cl_2. The solvent was removed from the eluate by oil pump vacuum to give **2c**[s7] as a white-yellow solid (0.018 g, 0.020 mmol, 51%).

Crystallography. A. A hexanes solution of **1b** (partially sealed container) was refrigerated and allowed to slowly concentrate by evaporation over the course of 3 d. The tan blocks were collected, and data were obtained as outlined in Table s1. Cell parameters were determined from 45 data frames taken at widths of 1° and refined with 6586 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX-3.[s8] Data were corrected for Lorentz and polarization factors, and crystal decay and absorption effects (using SADABS).[s9] Hydrogen atoms were placed in idealized positions and refined using a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. The absence of additional symmetry was confirmed using PLATON.[s10] The structure was refined (weighted least squares refinement on F^2) to convergence.[s11,s12]

B. Methanol was added to a concentrated diethyl ether solution of **4c** until the sample was opaque. Then diethyl ether was added until the sample was again homogeneous. The solution was refrigerated. After 5 d, yellow blocks were collected, and data were obtained as outlined in table s1. Cell parameters were determined from 45 data frames taken at widths of 1° and refined with 8637 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames using APEX3.[s8] Data were corrected for Lorentz and polarization factors, and crystal decay and absorption effects (using SADABS).[s9] Hydrogen atoms were placed in idealized positions and refined using a riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated ellipsoids on C32 and C33 suggested disorder which was modeled successfully between two positions (occupancy ratio 0.65:0.35). Appropriate restraints were added to keep the bond distances and thermal ellipsoids of the disordered atoms meaningful. The absence of additional symmetry or void were confirmed using PLATON.[s10] The structure was refined (weighted least squares refinement on F^2) to convergence.[s11,s12]

C. Diethyl ether was added to a small quantity of **1c**·2O. Then CH_2Cl_2 was added until the **1c**·2O dissolved. The sample was stored (partially sealed container) at 4 °C. After 21 d, a twinned colorless block was collected and data were obtained as outlined in table s1. Cell parameters were determined from 45 data frames were taken at widths of 1°. CELL_NOW was used to identify a 180° rotational twin. Efforts were made to resolve overlapping by collecting data at a crystal/detector distance of 120 mm. Trials were made to integrate the data with both twins. Application of TWINABS (for absorption corrections) followed by refinement gave a completeness below 90%, with many reflections discarded (by SAINT in APEX 3 or TWINABS). Thus, only the major component of the twin was used. TWINROTMAT in PLATON[s10] showed the twin matrix, which closely matched that from CELL_NOW. The former was used for the final refinement. Integrated intensity information for each reflection was obtained by reduction of the data frames with APEX3.[s8] Data were corrected for Lorentz and polarization factors, and crystal decay and absorption effects (using SADABS).[s9] Four molecules of water were present for every molecule of **1c**·2O. Hydrogen atoms were placed in idealized positions and were refined using a riding model. While some of the water hydrogen atoms could be located from difference Fourier maps, others were fit into a hydrogen bonding motif, and this aspect of the structure should not be further analyzed. All non-hydrogen atoms were refined with anisotropic thermal parameters. The absence of additional symmetry or voids was confirmed using PLATON. The structure was refined (weighted least squares refinement on F^2) to convergence[s11,s12] and a completeness of 98.5%.

Table s1. Summary of crystallographic data.

Complex	**1b**	**1c**$\cdot$2O$\cdot$(H_2O)$_4$	**4c**
Empirical formula	$C_{36}H_{72}As_2$	$C_{42}H_{92}As_2O_6$	$C_{42}H_{84}As_2Cl_2Pt$
Formula weight	654.77	842.99	1004.92
Temperature [K]	110.00	110.00	110.00
Diffractometer	Bruker Venture	Bruker Venture	Bruker Venture
Wavelength [Å]	1.54178	1.54178	1.54178
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1$/n
Unit cell dimensions			
a [Å]	9.2624(6)	8.6319(6)	16.3117(5)
b [Å]	9.3808(6)	13.4245(10)	13.9045(5)
c [Å]	25.6699(17)	20.7781(15)	20.1180(6)
α [°]	85.931(2)	72.297(2)	90
β [°]	83.106(2)	84.548(2)	91.2943(13)
γ [°]	61.125(2)	88.073(2)	90
Volume [Å^3]	1938.8(2)	2283.3(3)	4561.7(3)
Z	2	2	4
ρ_{calcd} [Mg m^{-3}]	1.122	1.226	1.463
μ [mm^{-1}]	2.255	2.123	8.619
F(000)	708	916	2056
Crystal size [mm^3]	0.057 x 0.014 x 0.01	0.162 x 0.124 x 0.085	0.042 x 0.031 x 0.03
Θ range [°]	3.469 to 65.585	3.456 to 65.565	3.527 to 69.989
Index ranges	$-10 \le h \le 10$	$-10 \le h \le 9$	$-19 \le h \le 19$
	$-11 \le k \le 11$	$-15 \le k \le 15$	$-16 \le k \le 15$
	$-30 \le l \le 30$	$-24 \le l \le 24$	$-24 \le l \le 24$
Reflections collected	26789	30552	59120
Independent reflections	6586 [R(int) = 0.0347]	7756 [R(int) = 0.0545]	8637 [R(int) = 0.0510]
Max. and min. transmission	0.3795 and 0.2800	0.4649 and 0.3677	0.3520 and 0.1685
Data / restraints / parameters	6586 / 0 / 343	7756 / 0 / 458	8637 / 97 / 443
Goodness-of-fit on F^2	1.048	1.169	1.060
Final R indices [I>2σ(I)]	*R*1 = 0.0314, wR2 = 0.0855	*R*1 = 0.0678, wR2 = 0.1677	*R*1 = 0.0265, wR2 = 0.0669
R indices (all data)	*R*1 = 0.0341, *w*R2 = 0.0874	*R*1 = 0.0717, wR2 = 0.1707	*R*1 = 0.0288, wR2 = 0.0688
Largest diff. peak and hole [eÅ^{-3}]	0.949 and -0.398	1.141 and -0.609	1.618 and -0.748

Notes and References

(s1) IR spectra show that **1a**$\cdot$2O readily hydrates under ambient Texas atmospheres, as supported by the isolation of crystalline **1a**$\cdot 2O\cdot(H_2O)_4$ from CH_2Cl_2/ethyl ether. Samples may be dried using 3Å molecular sieves.

(s2) The ^{13}C NMR spectrum shows more than the expected number of signals and the basis for this phenomenon remains under investigation. The macroscopic composition seems assured from the crystal structure and microanalysis.

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