Supporting Information

Transition Metal-mediated Donor-acceptor Coordination of Low-oxidation State Group 14 Element Halides

Anindya K. Swarnakar, Michael J. Ferguson, Robert McDonald, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2.

Contents

Table S1. Crystallographic data for compound **1**

A. Crystal Data	
formula	$C_{26}H_{27}Cl_2GeO_5P_2RhW$
formula weight	911.66
crystal dimensions (mm)	0.27×0.14×0.11
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	8.9888 (3)
b (Å)	24.3719 (7)
c (Å)	14.4140 (4)
β (deg)	104.3064 (3)
V (Å^3)	3059.81 (16)
Z	4
ρ_{calcd} (g cm^{-3})	1.979
μ (mm^{-1})	5.572
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	56.65
total data collected	28051 ($-11 \leq h \leq 11$, $-32 \leq k \leq 31$, $-19 \leq l \leq 19$)
independent reflections	7477 ($R_{\text{int}} = 0.0162$)
number of observed reflections (*NO*)	7036 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6400–0.3265
data/restraints/parameters	7477 / 0 / 351
goodness-of-fit (S)[e] [all data]	1.058
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0160
wR_2 [all data]	0.0379
largest difference peak and hole	1.032 and –0.480 e Å^{-3}

[a] Obtained from least-squares refinement of 9932 reflections with $4.44° < 2\theta < 56.48°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. Gould,

O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen,

[d]G. M. Sheldrick, *Acta Crystallogr.*2008, **A64**, 112–122.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0187P)^2 + 1.4453P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2. Crystallographic data for compound **2**

A. Crystal Data

formula	$C_{26.25}H_{27.5}Cl_{2.5}O_5P_2RhSnW$
formula weight	979.00
crystal dimensions (mm)	0.27 × 0.02 × 0.02
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	15.3972 (2)
b (Å)	9.0453 (1)
c (Å)	23.3877 (3)
β (deg)	90.5374 (12)
V (Å^3)	3257.12 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.996
μ (mm^{-1})	19.58

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	145.17
total data collected	21691 ($-19 \leq h \leq 18$, $-11 \leq k \leq 11$, $-28 \leq l \leq 28$)
independent reflections	6344 (R_{int} = 0.0781)
number of observed reflections (*NO*)	5092 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[d,e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8514–0.1190
data/restraints/parameters	6344 / 0 / 347
goodness-of-fit (S)[f] [all data]	1.031
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0345
wR_2 [all data]	0.0868
largest difference peak and hole	1.130 and –1.373 e Å^{-3}

[a] Obtained from least-squares refinement of 9963 reflections with 6.84° < 2θ < 143.88°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. Gould,

O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen,

[d] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.

[e] Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent dichloromethane chlorine or carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure (P. van der Sluis and A. L. Spek, *Acta Crystallogr.* 1990, **A46**, 194–201) as implemented in *PLATON* (A.L. Spek, *Acta Crystallogr.* 1990, **A46,** C34; A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7–13. *PLATON* - a multipurpose crystallographic tool. UtrechtUniversity, Utrecht, The Netherlands). A total solvent-accessible void volume of 225.6Å^3 with a total electron count of 43 (consistent with one molecule of solvent CH_2Cl_2, or 0.25 molecule per formula unit of the metal complex molecule) was found in the unit cell.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0403P)^2 + 0.9612P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S3. Crystallographic data for compound **3**

A. Crystal Data

formula	$C_{21}H_{27}Cl_2P_2PbRh$
formula weight	722.36
crystal dimensions (mm)	0.09 × 0.08 × 0.07
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	17.346 (5)
b (Å)	15.351 (4)
c (Å)	18.164 (5)
β (deg)	95.470 (3)
V (Å^3)	4814 (2)
Z	8
ρ_{calcd} (g cm^{-3})	1.993
μ (mm^{-1})	8.030

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.52
total data collected	41795 ($-22 \leq h \leq 22$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$)
independent reflections	11064 ($R_{int} = 0.0573$)
number of observed reflections (*NO*)	8280 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7619–0.5292
data/restraints/parameters	11064 / 0 / 495
goodness-of-fit (S)[d] [all data]	1.120
finalR indices[e]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0364
wR_2 [all data]	0.0816
largest difference peak and hole	1.992 and –1.824 e Å^{-3}

[a] Obtained from least-squares refinement of 9990 reflections with $4.50° < 2\theta < 53.30°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[d] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.

[d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; w =

$[\sigma^2(F_o^2) + (0.0316P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3)$.

[e] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S4. Crystallographic data for compound **4**

A. Crystal Data

formula	$C_{48}H_{43}BF_{18}P_2Rh$
formula weight	1137.48
crystal dimensions (mm)	0.26×0.20×0.16
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	12.2135 (3)
b (Å)	12.5991 (3)
c (Å)	17.0103 (4)
α (deg)	80.6961 (10)
β (deg)	81.3382 (8)
γ (deg)	75.2500 (8)
V (Å^3)	2481.49 (10)
Z	2
ρ_{calcd} (g cm^{-3})	1.522
μ (mm^{-1})	4.305

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.46
total data collected	17405 ($-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-21 \leq l \leq 20$)
independent reflections	9416 (R_{int} = 0.0129)
number of observed reflections (*NO*)	9241 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d.e])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6786–0.4912
data/restraints/parameters	9416 / 0 / 716
goodness-of-fit (*S*)[f] [all data]	1.026
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0319
wR_2 [all data]	0.0860
largest difference peak and hole	1.112 and –0.806 e Å^{-3}

[a] Obtained from least-squares refinement of 9844 reflections with $8.46° < 2\theta < 144.24°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3–8. (*SHELXT-2014*)

[d] G. M. Sheldrick, G. M. *Acta Crystallogr.*2015, **C71**, 3–8. (*SHELXL-2014*)

[e] Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent hexane carbon atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedureas implemented in *PLATON* (A. L. Spek,. *Acta Crystallogr.*2015, **C71**, 9–18. *PLATON* - a multipurpose crystallographic tool. UtrechtUniversity, Utrecht, The Netherlands). A total solvent-accessible void volume of 221Å^3 with a total electron count of 50 (consistent with 1 molecule of solvent hexane, or 0.5 molecules per formula unit of the rhodium complex) was found in the unit cell.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0493P)^2 + 2.1386P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5. Crystallographic data for compound **5**

A. Crystal Data	
formula	$C_{44}H_{73}Cl_2GeO_5P_2PtW$
formula weight	1266.39
crystal dimensions (mm)	0.29×0.09×0.06
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	10.172 (2)
b (Å)	12.807 (3)
c (Å)	20.478 (4)
α (deg)	105.848 (2)
β (deg)	103.959 (2)
γ (deg)	93.004 (3)
V (Å^3)	2470.6 (8)
Z	2
ρ_{calcd} (g cm^{-3})	1.702
μ (mm^{-1})	5.964
B. Data Collection and Refinement Conditions	
diffractometer	BrukerD8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.18
total data collected	22384 ($-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-26 \leq l \leq 26$)
independent reflections	11338 ($R_{\text{int}} = 0.0148$)
number of observed reflections (*NO*)	9930 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.7960–0.3812
data/restraints/parameters	11338 / 3[d] / 534
goodness-of-fit (S)[e] [all data]	1.117
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0212
wR_2 [all data]	0.0603
largest difference peak and hole	1.248 and –1.042 e Å^{-3}

[a] Obtained from least-squares refinement of 9783 reflections with 4.46° < 2θ < 55.04°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] G. M. Sheldrick, *ActaCrystallogr.*2008, **A64**, 112–122.

[d] The C–C distances within the minor component of the disordered solvent hexane molecule were restrained to be approximately equal by use of the *SHELXL* **SADI** instruction.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0333P)^2 + 0.5140P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S6. Crystallographic data for compound **6**

A. Crystal Data	
formula	$C_{41}H_{66}Cl_2O_5P_2PtSnW$
formula weight	1355.58
crystal dimensions (mm)	0.23×0.18×0.09
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	14.8910 (4)
b (Å)	16.3240 (4)
c (Å)	22.1599 (6)
V (Å^3)	5386.6 (2)
Z	4
ρ_{calcd} (g cm^{-3})	1.672
μ (mm^{-1})	5.379
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	54.98
total data collected	47820 ($-19 \leq h \leq 19$, $-21 \leq k \leq 21$, $-28 \leq l \leq 28$)
independent reflections	12339 ($R_{\text{int}} = 0.0289$)
number of observed reflections (*NO*)	11780 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2013*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6982–0.4584
data/restraints/parameters	12339 / 18[d] / 512
Flack absolute structure parameter[e]	0.0093(19)
goodness-of-fit (S)[f] [all data]	1.005
final R indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0176
wR_2 [all data]	0.0404
largest difference peak and hole	0.737 and –0.323 e Å^{-3}

[a] Obtained from least-squares refinement of 9906 reflections with $4.44° < 2\theta < 51.62°$.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.

[d] Distances within the disordered solvent n-hexane molecule were restrained to idealized target

distances during refinement: d(C1SA–C2SA) = d(C2SA–C3SA) = d(C3SA–C4SA) = d(C4SA–C5SA) = d(C5SA–C6SA) = d(C1SB–C2SB) = d(C2SB–C3SB) = d(C3SB–C4SB) = d(C4SA–C5SB) = d(C5SB–C6SB) = 1.50(1) Å; d(C1SA···C3SA) = d(C2SA···C4SA) = d(C3SA···C5SA) = d(C4SA···C6SA) = d(C1SB···C3SB) = d(C2SB···C4SB) = d(C3SB···C5SB) = d(C4SB···C6SB) = 2.45(1) Å.

[e] H. D. Flack, *Acta Crystallogr.* 1983, **A39**, 876–881; H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* 1999, **A55**, 908–915; H.D. Flack, G. Bernardinelli, *J. Appl. Cryst.* 2000, **33**, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0115P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.