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# Reactions of 'GaI' with organometallic transition metal halides

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Dedicated to Professor Tony Downs in recognition of his numerous contributions to main group chemistry, not least to the chemistry of gallium.

### Abstract

Two approaches towards the synthesis of phosphine ligated half-sandwich complexes  $[(\eta^x - C_x H_x)M(PR_3)_2GaI_2]_n$  containing diiodogallyl ligands have been investigated. Insertion of 'GaI' into the Mo–I bond of  $(\eta^7 - C_7H_7)Mo(CO)_2I$  has been shown to yield the crystallographically characterized dimeric complex  $[(\eta^7 - C_7H_7)Mo(CO)_2GaI_2]_2$  (2). Attempts to substitute the carbonyl ligands by the phosphine ligand dppe [dppe = bis(diphenylphosphino)ethane] have been shown instead to yield the sparingly soluble complex  $[(\eta^7 - C_7H_7)Mo(CO)_2GaI_2]_2(\mu$ -dppe) (3) in which the phosphine bridges two  $[(\eta^7 - C_7H_7)Mo(CO)_2GaI_2]$  units via a pair of  $P \rightarrow Ga$ donor/acceptor bonds. By contrast, attempts to insert 'GaI' directly into the metal-halogen bond of phosphine ligated complexes such as  $(\eta^5 - C_5H_5)Ru(PPh_3)_2Cl$  or  $(\eta^5 - C_5H_5)Ru(dppe)Cl$  have been shown to result in the formation of the tetraiodogallate species  $(\eta^5 - C_5H_5)Ru(PPh_3)_2(\mu-I)GaI_3$  (5) and  $[(\eta^5 - C_5H_5)Ru(dppe)]^+[GaI_4]^-$  (7). © 2007 Elsevier B.V. All rights reserved.

Keywords: Gallium; Insertion; Substitution; Phosphine ligands; Ruthenium; Molybdenum

### 1. Introduction

Investigation of the chemistry of transition metal complexes featuring low coordinate group 13 ligands has been the main focus of considerable recent research interest [1]. In particular, the nature of the interaction between the ligand and the transition metal centre in diyl systems  $[L_nM(ER)]$  (E = B-Tl) has been the subject of considerable debate [2]. The bonding descriptions proposed for complexes such as (CO)<sub>4</sub>Fe(GaAr) [Ar = C<sub>6</sub>H<sub>3</sub>(2,4,6<sup>-i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>-2,6] featuring either multiple bonds (i.e.  $L_nM=ER$ or  $L_nM=ER$ ) or simple donor-acceptor interactions (i.e.,  $L_nM \leftarrow ER$ ) reflect not only the fundamental questions of structure and bonding posed by such systems but also the scarcity of structural data available.

Within this area we have been interested in synthesizing cationic two coordinate divides  $[L_n M(ER)]^+$  (for E = B, Ga or In) [3–5]. DFT calculations have revealed that the positive charge is located primarily on the group 13 centre in such systems, resulting in a significant  $M \rightarrow E$  back-bonding component and M=E multiple bond character [6]. From a synthetic point of view we have previously demonstrated that *halide abstraction* chemistry is a viable route to cationic metal complexes featuring group 13 ligands {e.g.  $[(\eta^5-C_5Me_5)Fe(CO)_2](=BMes)]^+[BAr_4^f]^$ and  $[(\eta^5 - C_5 H_5)Fe(CO)_2(=BNCy_2)]^+[BAr_4^f]^-$ ,  $Ar^f = C_6 H_3$ - $(CF_3)_2$ -3,5 [3,4]. In recent work we have sought to extend this approach to the heavier group 13 elements, in particular with a view to exploring the structural and reaction chemistry of cationic two-coordinate gallanediyl complexes [5]. Of particular interest in this respect are electron-rich transition metal fragments  $(L_n M)$  bearing ancillary phosphine ligands which would be expected to offer not only enhanced steric shielding, but also increased  $\pi$  backbonding to the cationic gallium centre formed on halide

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Scheme 1. Strategies for the generation of cationic systems containing group 13 donor ligands utilizing GaI in the synthesis of key precursors.

abstraction. Central to this approach is ready access to a range of halo-substituted precursors featuring three-coordinate gallium centres and bearing ancillary phosphine ligands at the metal centre (see Scheme 1).

We have previously demonstrated for iron-containing systems that clean substitution of the carbonyl ligands in the complex  $[(\eta^5-C_5Me_5)Fe(CO)_2GaI_2]_2$  is possible; prolonged photolysis in the presence of dppe [dppe = 1.2-bis(diphenylphosphino)ethane] vields  $(\eta^5-C_5Me_5)$ - $Fe(dppe)GaI_2$  in which the phosphine ligand binds to the iron centre in a chelating fashion [7]. Herein we report attempts to develop routes to related ruthenium and molybdenum complexes. During the course of this study two parallel synthetic approaches to these phosphine-containing halogallyl species have been examined: (i) a two-step process involving initial insertion of 'GaI' into the metal-halogen bond of a metal carbonyl complex followed by substitution of the CO ligands at the metal centre by phosphines; and (ii) direct insertion of 'GaI' into the metal-halogen bond of a metal complex featuring ancillary phosphine ligands (Scheme 1).

### 2. Experimental

### 2.1. General

All manipulations were carried out under a nitrogen or argon atmosphere using standard Schlenk line or dry box techniques. Solvents were pre-dried over sodium wire (hexanes, toluene) or molecular sieves (dichloromethane) and purged with nitrogen prior to distillation. Hexanes (potassium), toluene (sodium), and dichloromethane (calcium hydride) were then distilled from the appropriate drying agent before use. Dichloromethane- $d_2$  (Goss) was degassed and dried over molecular sieves prior to use. Starting materials, 'GaI' [8], ( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Mo(CO)<sub>2</sub>I (1) [9], ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>Cl (4) [10] and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(dppe)Cl (6) [11] were prepared by literature routes. NMR spectra were measured on a Bruker AM-400 or Jeol Eclipse 300 Plus FT-NMR spectrometer; residual signals of solvent were used for reference for <sup>1</sup>H and <sup>13</sup>C NMR, while <sup>31</sup>P NMR spectra was referenced with respect to 85% H<sub>3</sub>PO<sub>4</sub>. Infrared were measured on a Nicolet 500 FT-IR spectrometer. Mass spectra were measured by the EPSRC National Mass Spectrometry Service Centre, University of Wales Swansea. The presence of solvent molecules in the crystal-line lattices of compounds **3**, **5** and **7** precluded reproducible elemental microanalyses.

*Abbreviations*: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad; st, strong; md, medium; w, weak; sh, shoulder.

### 2.2. Syntheses

### 2.2.1. $[(\eta^7 - C_7 H_7) Mo(CO)_2 GaI_2]_2$ (2)

To a suspension of 'GaI' prepared by sonicating gallium (1.057 g, 15.16 mmol) and I<sub>2</sub> (1.925 g, 7.58 mmol) in toluene (50 cm<sup>3</sup>) for 16 h at 30 °C was added a solution of 1 (2.003 g, 5.41 mmol) in toluene  $(100 \text{ cm}^3)$ . The reaction mixture was stirred at 20 °C for 72 h leading to the formation of a red solution and dark purple precipitate. The precipitate was isolated, recrystallized from dichloromethane  $(300 \text{ cm}^3)$  by cooling to -30 °C, isolated by filtration and dried in vacuo. Crystals suitable for X-ray diffraction were obtained at -30 °C from a concentrated solution in dichloromethane. Yield: 1.108 g 36%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm H}$  5.60 (s, 14H, CH of  $\eta^7$ -C<sub>7</sub>H<sub>7</sub>). <sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm C}$  93.5 (CH of  $\eta^7$ -C<sub>7</sub>H<sub>7</sub>), carbonyl carbons not observed. IR (thin film  $CD_2Cl_2$ , cm<sup>-1</sup>):  $v_{CO}$ 2001 st, 1952 st. Mass spec. (CI -ve): m/z (%) 694.6 (3)  $[(\eta^{7}-C_{7}H_{7})Mo(CO)_{2}GaI_{3}]^{-}$ , 567.7 (2)  $[(\eta^{7}-C_{7}H_{7})Mo (CO)_2GaI_2^{-};$  (EI): m/z (%) 567.7 (1)  $[(\eta^7-C_7H_7)Mo(CO)_2^{-}]$  $GaI_2$ <sup>+</sup>, 539.7 (1)  $[(\eta^7 - C_7 H_7)Mo(CO)GaI_2$ <sup>+</sup>, 511.7 (2)  $[(\eta^7 - C_7 H_7)MoGaI_2]^+$ . Exact mass (CI -ve): Calc. for  $[(\eta^7 - C_7 H_7)MoGaI_2]^+$ . C<sub>7</sub>H<sub>7</sub>)Mo(CO)GaI<sub>2</sub>]<sup>-</sup> 539.6902; measd. 539.6902. Elemental Anal. Calc. for C<sub>18</sub>H<sub>14</sub>Ga<sub>2</sub>I<sub>4</sub>Mo<sub>2</sub>O<sub>4</sub>: C, 19.08; H, 1.25. Measd.: C, 18.99; H, 1.11.

2.2.2.  $[(\eta^7 - C_7 H_7) Mo(CO)_2 GaI_2]_2(\mu - dppe)$  (3)

A solution of dppe (0.779 g, 1.96 mmol) in toluene  $(150 \text{ cm}^3)$  was added to a solution of 2 (1.108 g, 0.98 mmol) in toluene (150 cm<sup>3</sup>) at 20 °C with the immediate formation of a light red precipitate. The precipitate was extracted into dichloromethane (500 cm<sup>3</sup>; sparingly soluble) and filtered; the resulting dark orange solution was concentrated in *vacuo*, and a red solid obtained by cooling to -30 °C. Crystals suitable for X-ray diffraction were obtained from the concentrated solution at -30 °C. Yield: 0.383 g 26%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm H}$  2.55 (m, 2H, CH<sub>2</sub> of dppe), 2.92 (m, 2H, CH<sub>2</sub> of dppe), 5.18 (s, 7H,  $\eta^7$ -C<sub>7</sub>H<sub>7</sub>), 7.23 (m, 8H, aromatic CH of dppe), 7.49 (m, 8H, aromatic CH of dppe), 7.62 (m, 4H, aromatic CH of dppe). <sup>31</sup>P NMR (122 MHz,  $CD_2Cl_2$ ):  $\delta_P - 28$  (broad). IR (thin film  $CD_2Cl_2$ , cm<sup>-1</sup>): v<sub>CO</sub> 1982 st, 1928 st. Mass spec. (EI): m/z (%) 712.0 (5)  $[(\eta^7 - C_7 H_7)Mo(CO)_2Ga(dppe)]^+$ . The extremely low solubility of 3 in compatible solvents precluded the measurement of reliable <sup>13</sup>C NMR spectra.

2.2.3.  $(\eta^5 - C_5 H_5) Ru(PPh_3)_2(\mu - I) GaI_3$  (5)

To a suspension of 'GaI' [prepared as described above from gallium (0.272 g, 3.901 mmol) and  $I_2$  (0.499 g, 3.901 mmol)1.966 mmol was added a solution of 4 (0.939 g, 1.293 mmol) in toluene  $(100 \text{ cm}^3)$ . The reaction mixture stirred at 20 °C for 16 h. with the formation of an orange solution and orange precipitate. The solid was recrystallized from dichloromethane by cooling to -30 °C. Crystals suitable for X-ray diffraction were obtained at -30 °C from a concentrated solution in dichloromethane. Yield: 0.682 g 42%. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm H}$  4.61 (5H, s, CH of n<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>), 7.09 (12H, aromatic CH of PPh<sub>3</sub>), 7.27 (12H, aromatic CH of PPh<sub>3</sub>), 7.39 (6H, aromatic CH of PPh<sub>3</sub>). <sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm C}$  80.2 (CH of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 128.3 (aromatic CH of PPh<sub>3</sub>), 129.9 (aromatic CH of PPh<sub>3</sub>), 133.8 (aromatic CH of PPh<sub>3</sub>), 137.5 (aromatic *ipso*-C of PPh<sub>3</sub>). <sup>31</sup>P NMR (122 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_P$  35. Mass spec. (EI): m/z (%) 556.2 (2)  $[(\eta^5 - C_5H_5)Ru(PPh_3)I]^+$ , 449.7 (30)  $[GaI_3]^+$ , 322.8 (35)  $[GaI_2]^+$ .

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Crystallographic data for 2, 3, 5, 7, and 8

	2	$3\cdot 2.5(CH_2Cl_2)$	$\textbf{5} \cdot 0.5 (C_7 H_8)$	$\textbf{7} \cdot 2(CH_2Cl_2)$	8
Empirical formula	C <sub>18</sub> H <sub>14</sub> Ga <sub>2</sub> I <sub>4</sub> Mo <sub>2</sub> O <sub>4</sub>	C <sub>46.50</sub> H <sub>43</sub> Cl <sub>5</sub> Ga <sub>2</sub> I <sub>4</sub> O <sub>4</sub> Mo <sub>2</sub> P <sub>2</sub>	C44.50H39GaI4P2Ru	C33H33Cl4GaI4P2Ru	$C_{62}H_{58}Ga_2I_8P_4Ru_2$
CCDC reference	634453	634454	634455	634456	634457
Formula weight	1133.21	1743.92	1314.09	1311.72	2283.74
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	$P2_1/n$	$P2_1/n$
Unit cell dimensions					
a (Å)	7.8446(16)	10.385(2)	22.862(5)	16.088(3)	13.126(3)
b (Å)	9.0483(18)	16.850(3)	13.190(3)	15.257(3)	17.613(4)
<i>c</i> (Å)	18.888(4)	17.935(4)	29.374(6)	17.437(4)	14.962(3)
α (°)	90.52(3)	65.63(3)	90	90	90
β (°)	93.93(3)	82.01(3)	102.71(3)	98.82	100.64(3)
γ (°)	105.31(3)	86.40(3)	90	90	90
Volume (Å <sup>3</sup> )	1289.6(4)	2830.9(10)	8641(3)	4229.5(15)	3399.4(12)
$Z, D_{\text{calc}} (\text{Mg/m}^3)$	2, 2.918	2, 2.046	8, 2.020	4, 2.060	2, 2.231
Absorption coefficient (mm <sup>-1</sup> )	7.827	3.887	3.936	4.265	4.984
$F_{000}$	1024	1654	4984	2464	2128
Crystal size (mm)	$0.25\times0.10\times0.05$	$0.18 \times 0.15 \times 0.11$	$0.10\times0.10\times0.06$	$0.35 \times 0.30 \times 0.20$	$0.15 \times 0.10 \times 0.08$
$\theta$ Range for data collection (°)	2.98-26.00	3.00-26.00	2.94-24.99	2.92-30.00	2.99-25.00
Index ranges					
h	-9 to 9	-12 to 12	-26 to 26	-22 to 22	-15 to 15
k	-11 to 11	-20 to 20	-15 to 15	-21 to 21	-20 to 20
1	-22 to 23	-21 to 21	-34 to 34	-24 to 24	-17 to 17
Reflections collected	8896	20483	13338	23357	11181
Independent reflections $[R_{int}]$	4947 [0.0327]	11030 [0.0374]	7447 [0.0433]	12261 [0.0212]	5940 [0.0425]
Completeness to $\theta_{\text{maximum}}$ (%)	97.3	99.2	97.7	99.3	99.2
Absorption correction	SORTAV	SORTAV	SORTAV	SORTAV	SORTAV
Maximum and minimum transmission	0.778, 0.521	0.659, 0.504	0.867, 0.644	0.475, 0.310	0.856, 0.713
Data/restraints/parameters	4947/0/271	11030/48/645	7447/11/469	12261/0/406	5940/0/394
Goodness-of-fit on $F^2$	1.030	1.012	1.080	1.016	1.029
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0309,$	$R_1 = 0.0424, wR_2 = 0.0919$	$R_1 = 0.0604,$	$R_1 = 0.0380,$	$R_1 = 0.0692,$
	$wR_2 = 0.0645$		$wR_2 = 0.1438$	$wR_2 = 0.032$	$wR_2 = 0.1671$
R indices (all data)	$R_1 = 0.0400,$	$R_1 = 0.0609, wR_2 = 0.0998$	$R_1 = 0.0909,$	$R_1 = 0.0508,$	$R_1 = 0.1011,$
	$wR_2 = 0.0683$		$wR_2 = 0.1587$	$wR_2 = 0.082$	$wR_2 = 0.1845$
Largest difference in peak and hole (e $Å^{-3}$ )	0.747 and -1.175	1.569 and -0.920	1.313 and -2.670	1.695 and -2.277	1.612 and -1.499

## 2.2.4. $[(\eta^5 - C_5 H_5) Ru(dppe)]^+ [GaI_4]^-$ (7)

To a suspension of 'GaI' (prepared as described above from gallium (0.581 g, 8.33 mmol) and I<sub>2</sub> (1.057 g, 4.17 mmol)) was added a solution of 6 (0.499 g, 0.83 mmol) in toluene ( $80 \text{ cm}^3$ ). The reaction mixture was stirred at room temperature for 72 h with the formation of a pale yellow solution and yellow precipitate. The solution was filtered, concentrated in vacuo, and a yellow solid was obtained by cooling to -30 °C. Crystals suitable for X-ray diffraction were obtained by layering a toluene solution with hexanes and cooling to -30 °C. Yield: 0.121 g 13%.<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm H}$  2.51 (2H, m, CH<sub>2</sub>) of dppe), 2.59 (2H, m, CH<sub>2</sub> of dppe), 4.86 (5H, s, CH of  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>), 7.16 (8H, aromatic CH of Ph), 7.28 (8H, aromatic CH of Ph), 7.69 (4H, aromatic CH of Ph). <sup>13</sup>C NMR (76 MHz,  $CD_2Cl_2$ ):  $\delta_C$  21.2 (CH<sub>2</sub> of dppe), 79.7 (CH of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), 128.8 (aromatic CH of Ph), 129.9 (aromatic CH of Ph), 130.7 (aromatic CH of Ph), 134.1 (aromatic *ipso*-C of Ph). <sup>31</sup>P NMR (122 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta_{\rm P}$  76. Mass spec (EI): m/z (%) 761.0 (2)  $[(\eta^5 - C_5 H_5) Ru$ - $(dppe)GaI]^+, 692.1 (64) [(\eta^5-C_5H_5)Ru(dppe)I]^+, 565.2$ (100)  $[(\eta^5-C_5H_5)Ru(dppe)]^+$ . Exact mass (EI): calcd. for  $[(\eta^5 - C_5 H_5) Ru(dppe) GaI]^+$  760.9089; measd. 760.9089. A small amount (<5 mg) of a dark orange crystalline material was also obtained from the layering the structure was solved by X-ray diffraction to be the isomeric product  $[(\eta^{5}-C_{5}H_{5})Ru(GaI_{4})(\mu-dppe)]_{2}$  (8).

### 2.3. Crystallographic method

Data was collected on an Enraf Nonius Kappa CCD diffractometer equipped with a Mo K $\alpha$  radiation source  $(\lambda = 0.71073 \text{ Å})$ . Data collection and cell refinement were carried out using DENZO and COLLECT, and structure solution and refinement (by full-matrix least-squares) using shelxs-97 and shelxl-97, respectively [12]. Empirical absorption corrections were carried out using SORTAV [12]. Details of the data collection, structure solution and refinement for 2, 3, 5, 7 and 8 can be found in Table 1; relevant bond lengths and angles are included in the figure captions. Complete details of all structures have been deposited with the CCDC (reference numbers as listed in Table 1) and are included in the supporting information. The disordered solvent molecules in the asymmetric units of 3 and 5 (two and a half molecules of dichloromethane, and half a molecule of toluene, respectively) were modelled as described in the

CIF. The disordered  $GaI_4$  unit in 8 was modelled with two positions for each atom with half occupancy; I(5) sits on a centre of inversion.

### 3. Results and discussion

Two possible synthetic pathways towards systems of the type  $[(\eta^x-C_xH_x)M(PR_3)_2GaI_2]_n$  have been investigated during this study (Scheme 1). Route 1 involves a two-step synthesis via insertion of 'GaI' into the metal-halogen bond of a metal carbonyl precursor followed by substitution of the CO ligands by phosphines. Following this strategy, reaction of  $(\eta^7-C_7H_7)Mo(CO)_2I$  with 'GaI' proceeds as expected with insertion of 'GaI' into the Mo–I bond yielding the desired complex  $[(\eta^7-C_7H_7)Mo(CO)_2GaI_2]_2$  in modest (36%) yield after recrystallization from dichloromethane (Scheme 2).

NMR data for 2 are consistent with a formulation containing a single environment for the  $C_7H_7$  ring protons; additionally, mass spectrometry data provides evidence for a GaI<sub>2</sub>-containing species. However, as with related iron-containing systems, definitive identification of a metal-gallium bond and of the state of aggregation of the diiodogallyl complex were reliant on crystallographic methods (Fig. 1). The molecular structure of 2 features dimeric  $[(\eta^7 - C_7 H_7)Mo(CO)_2GaI_2]_2$  units in which each  $(\eta^7 - C_7 H_7)Mo(CO)_2GaI_2$  fragment is linked to the other through the bridging iodine ligands of the  $Ga(\mu-I)_2Ga$  core. The coordination geometry about each gallium centre is somewhat distorted from tetrahedral, featuring Mo-Ga-I angles of 125.9(4)°, 120.0(3)° and 116.9(3)°, and I-Ga-I angles of 98.2(3)°, 98.6(4)° and 89.7(3)°. The narrower I-Ga-I angle of ca. 90° associated with the bridging iodine atoms finds precedent in the structures of related systems {e.g. 92.01(2)° in  $[(\eta^5-C_5Me_5)Fe(CO)_2GaI_2]_2$  [13]. The Mo-Ga bond length of 2.577(1) Å is unremarkable, being similar to those reported for the complexes ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)- $Mo(CO)_3GaI_2 \cdot Et_2O$  and  $cis-(Cp*Ga)_2Mo(CO)_4$  [2.582(2) and 2.554(1) Å, respectively [8,14].

The determination of the molecular structure of **2** confirms that insertion of 'GaI' is indeed a feasible pathway for synthesizing gallium-containing transition metal carbonyl complexes. Similar chemistry has also been reported by Green et al. in the synthesis of the closely related complex  $(\eta^7-C_7H_7)Mo(CO)_2GaI_2 \cdot thf$ , which was characterized by <sup>1</sup>H NMR [8]. In order to complete the two-step



Scheme 2. Synthesis of  $[(\eta^7-C_7H_7)Mo(CO)_2GaI_2]_2$  (2) and its subsequent reactivity towards dppe. Reagents and conditions: (i) 'GaI' (2.8 equiv.), toluene, 20 °C, 72 h, 36% isolated yield; (ii) dppe (2 equiv.), toluene, 20 °C, 10 min., 26% isolated yield.



Fig. 1. Structure of  $[(\eta^7-C_7H_7)Mo(CO)_2GaI_2]_2$  (2) with hydrogen atoms omitted for clarity and ORTEP ellipsoids set at 50% probability level. Relevant bond lengths (Å) and angles (°): Mo(1)-Ga(1) 2.577(1), Mo(1)-C(8) 2.010(6), Mo(1)-centroid 1.651(6), Ga(1)-I(1) 2.619(1), Ga(1)-I(2) 2.764(1), Ga(1)-I(2') 2.807(1), Mo(1)-Ga(1)-I(1) 125.9(4), Mo(1)-Ga(1)-I(2) 120.0(1), Mo(1)-Ga(1)-I(2') 116.9(1), I(1)-Ga(1)-I(2) 98.2(1), I(1)-Ga(1)-I(2') 98.6(1), I(2)-Ga(1)-I(2') 89.7(1). Symmetry transformations used to generate equivalent atoms: ': -x + 2, -y + 1, -z.

synthesis of  $[(\eta^7-C_7H_7)M(PR_3)_2GaI_2]_n$ , **2** was further reacted with the potentially chelating phosphine ligand dppe; photolytically or thermally initiated substitution reactions of  $(\eta^7 - C_7 H_7)M(CO)_2X$  with phosphines have been amply demonstrated in the literature [15]. However, on addition of dppe to 2 at room temperature, an immediate reaction resulted in the formation of a red precipitate, which was subsequently determined crystallographically to be the dinuclear species  $[(\eta^7 - C_7 H_7)Mo(CO)_2GaI_2]_2(\mu$ dppe) (3) (Scheme 2). Previous work with related iron-containing systems is consistent with initial formation of  $R_3P \rightarrow Ga(III)$  adducts, but has shown that subsequent photolysis can lead to migration of the phosphine donor from gallium to the transition metal upon loss of CO [7]. Attempts to photolytically induce an analogous phosphine migration for 3 were frustrated by its very sparing solubility in compatible organic solvents. Additionally, thermolysis of 3 invariably resulted in decomposition. Attempts

to ameliorate these problems, e.g. by the use of other phosphine donors are currently ongoing.

<sup>1</sup>H and <sup>31</sup>P NMR data for **3** are consistent with a gallium-bound phosphine containing species [broad resonance at  $\delta_{\rm P}$  -28 c.f. -41 for the analogous phosphorus centre in  $Cp*Fe(CO)(\mu-dppe)GaI_2$ ]. Additionally, the presence of strong infra-red bands at 1982 and 1928 cm<sup>-1</sup> implies retention of the Mo(CO)<sub>2</sub> fragment within the complex, and therefore that phosphine substitution has not occurred at the molybdenum centre. These spectroscopic inferences were confirmed by X-ray diffraction which revealed the structure of **3** as  $[(\eta^7 - C_7 H_7)Mo(CO)_2GaI_2]_2(\mu-dppe)$ (Fig. 2). The molecular structure of 3 features dppe acting as a bridging ligand between two  $(\eta^7 - C_7 H_7)Mo(CO)_2GaI_2$ units; the 1:2 dppe:Mo ratio in the product (c.f. the 2:1 reaction stoichiometry) is presumably driven by the insolubility of 3. The coordination geometry about the gallium centres is distorted tetrahedral with Mo-Ga-I angles of



Fig. 2. Structure of  $[(\eta^7-C_7H_7)Mo(CO)_2GaI_2]_2\mu$ -dppe (3) with hydrogen atoms and solvent molecules omitted for clarity and ORTEP ellipsoids set at 50% probability level. Relevant bond lengths (Å) and angles (°): Mo(1)-Ga(1) 2.577(1), Mo(1)-C(1) 1.997(5), Mo(1)-centroid 1.660(5), Ga(1)-I(1) 2.632(1), Ga(1)-I(2) 2.650(1), Ga(1)-P(1) 2.467(2), Mo(1)-Ga(1)-I(1) 118.2(1), Mo(1)-Ga(1)-I(2) 122.4(1), Mo(1)-Ga(1)-P(1) 119.8(1), I(1)-Ga(1)-I(2) 100.7(1), I(1)-Ga(1)-P(1) 97.9(1), I(2)-Ga(1)-P(1) 92.3(1).

118.21(3)° and 122.39(3)° and significantly narrower P–Ga–I angles of 92.3(4)° and 97.9(5)°. The Mo–Ga bond length of 2.581(1) Å is not significantly different that found in **2**.

An alternative synthetic approach to systems of the type  $[(\eta^{x}-C_{x}H_{x})M(PR_{3})_{2}GaI_{2}]_{n}$  was also examined (Scheme 1); route 2 involves direct insertion of 'GaI' into the metal halogen bond of a phosphine-ligated complex. On paper this route is advantageous in that it involves a single step synthesis from readily available starting materials of the type  $(n^5-C_5H_5)Ru(PR_3)$  hal. From the outset, relatively forcing conditions were employed (e.g. the use of a large excess of 'GaI'), since preliminary studies indicated that the use of fewer equivalents of 'GaI' at room temperature merely resulted in halide substitution reactions to give  $(\eta^5-C_5H_5)Ru(PR_3)_2I$  [16]. The reactions of both  $(\eta^5 C_5H_5$ )Ru(PPh\_3)<sub>2</sub>Cl (4, Scheme 3) and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru-(dppe)Cl (6, Scheme 4) with 'GaI' (4-10 equiv.) appear from <sup>31</sup>P NMR monitoring to follow a similar course. In each case one major product is formed which can be crystallized from the reaction supernatant by layering with hexanes and storage at -30 °C. In each case the <sup>31</sup>P NMR spectrum of the product is

In each case the <sup>31</sup>P NMR spectrum of the product is consistent with retention of the Ru(PR<sub>3</sub>)<sub>2</sub> moiety, however mass spectrometry data are consistent with ready fragmentation into GaI<sub>n</sub> and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(phosphine)<sub>n</sub>I containing units. In the reaction of **4** with 'GaI' (4 equiv.), the product isolated in modest (42%) yield was subsequently shown crystallographically to be ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ru(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -I)GaI<sub>3</sub> (**5**, Fig. 3). The molecular structure reveals a bis(phosphine) half sandwich complex containing a tetraiodogallate fragment coordinated to the ruthenium centre via a single bridging iodine atom. To our knowledge **5** represents the



Scheme 3. Synthesis of  $(\eta^5-C_5H_5)Ru(PPh_3)_2(\mu-I)GaI_3$  (5) from  $(\eta^5-C_5H_5)-Ru(PPh_3)_2CI$ . Reagents and conditions: (i) 'GaI' (2 equiv.), toluene, 20 °C, 4 h, 67% isolated yield; (ii) 'GaI' (4 equiv.), toluene, 20 °C, 16 h, 42% isolated yield.



Scheme 4. Synthesis of  $[(\eta^5-C_5H_5)Ru(dppe)]^+[GaI_4]^-$  (7) from  $(\eta^5-C_5H_5)Ru(dppe)Cl$ . Reagents and conditions: (i) 'GaI' (10 equiv.), toluene, 20 °C, 72 h, 13% isolated yield.



Fig. 3. Structure of  $(\eta^5-C_5H_5)Ru(PPh_3)_2(\mu-I)GaI_3$  (5) with hydrogen atoms and solvent molecule omitted for clarity and ORTEP ellipsoids set at 50% probability level. Relevant bond lengths (Å) and angles (°): Ru(1)–P(1) 2.345(4), Ru(1)–centroid 1.849(3), Ru(1)–I(1) 2.742(2), Ga(1)–I(1) 2.603(2), Ga(1)–I(2) 2.513(2), Ga(1)–I(3) 2.533(2), Ga(1)–I(4) 2.528(2), P(1)–Ru(1)–P(2) 102.6(2), Ru(1)–I(1)–Ga(1) 112.0(1), I(1)–Ga(1)–I(2) 103.7(1), I(1)–Ga(1)–I(3) 108.4(1), I(1)–Ga(1)–I(4) 111.6(1), I(2)–Ga(1)–I(3) 112.9(1), I(2)–Ga(1)–I(4) 111.4(1), I(3)–Ga(1)–I(4) 108.8(1).

first example of a transition metal complex containing a coordinated  $[GaI_4]^-$  ligand. Alternatively, 5 can be thought of as a Lewis acid/base adduct between  $(\eta^5-C_5H_5)Ru$ -(PPh<sub>3</sub>)<sub>2</sub>I and GaI<sub>3</sub>. The coordination geometry about the gallium centre is approximately tetrahedral with I-Ga-I bond angles of 103.7(1)°, 111.6(1)°, and 108.4(1)°. As expected the Ga-I bond associated with the bridging unit [2.603(2) Å] is considerably longer than the terminal Ga–I linkages [2.513(2), 2.533(2) and 2.528(2) Å]. Interestingly, the major product isolated from the reaction of 6 with 'GaI' (10 equiv.), despite having an analogous composition to 5, [i.e.  $(\eta^5-C_5H_5)Ru(dppe)(GaI_4)$ ], has been shown crystallographically to consist of discrete  $[(\eta^5-C_5H_5)-$ Ru(dppe)<sup>+</sup> and  $[GaI_4]$ <sup>-</sup> ions (7, Fig. 4). The shortest Ru $\cdots$ I contact [5.535 Å] is comfortably outside the sum of the respective Van der Waals radii [17], and contrasts with the Ru–I distance of 2.742(2) Å found for 5. In common with the related system  $[(\eta^5 - C_5 Me_5)Ru(PMe^i Pr_2)_2]^+$ [18], the trigonal planar geometry at the metal defined by the two phosphorus atoms and the cyclopentadienyl centroid [sum of the angles at ruthenium =  $358.8^{\circ}$  for 7] implies negligible secondary interactions (for example of ligand C-H bonds) with the 16-electron cationic ruthenium centre. The difference in coordinating ability for the tetraiodogallate ion with respect to the metal centres in 5 and 7 can conceivably be rationalized on the basis of reduced electrophilicity for the ruthenium centre found in conjunction with the more strongly  $\sigma$  basic dppe ligand.

A second product was also crystallized from the  $(\eta^5 - C_5H_5)Ru(dppe)Cl/GaI'$  reaction mixture in very low yield which has been shown crystallographically to be an isomer



Fig. 4. Structure of  $[(\eta^5-C_5H_5)Ru(dppe)]^+[GaI_4]^-$  (7) with hydrogen atoms and solvent molecules omitted for clarity and ORTEP ellipsoids set at 50% probability level. Relevant bond lengths (Å) and angles (°): Ru(1)–P(1) 2.286(1), Ru(1)–centroid 1.855(6), Ga(1)–I(1) 2.545(1), Ga(1)–I(2) 2.543(1), Ga(1)–I(3) 2.554(1), Ga(1)–I(4) 2.539(1), P(1)–Ru(1)–P(2) 86.5(1), I(1)–Ga(1)–I(2) 108.6(1), I(1)–Ga(1)–I(3) 109.1(1), I(1)–Ga(1)–I(4) 109.0(1), I(2)–Ga(1)–I(3) 109.8(1), I(2)–Ga(1)–I(4) 110.2(1), I(3)–Ga(1)–I(4) 110.2(1).



Fig. 5. Structure of  $[(\eta^5-C_5H_5)Ru(GaI_4)(\mu-dppe)]_2$  (8) with hydrogen atoms omitted for clarity and ORTEP ellipsoids set at 50% probability level. Relevant bond lengths (Å) and angles (°): Ru(1)–P(1) 2.338(3), Ru(1)–centroid 1.850(10), Ru(1)–I(1a) 2.748(9), Ga(1a)–I(1a) 2.590(8), Ga(1a)–I(2a) 2.532(4), Ga(1a)–I(3a) 2.523(4), Ga(1a)–I(4) 2.462(4), P(1)–Ru(1)–P(2) 98.0(1), Ru(1)–I(1a)–Ga(1a) 124.9(4), I(1a)–Ga(1a)–I(2a) 117.3(3), I(1a)–Ga(1a)–I(3a) 99.0(2), I(1a)–Ga(1a)–I(4) 109.0(2), I(2a)–Ga(1a)–I(3a) 114.7(2), I(2a)–Ga(1a)–I(4) 106.0(1), I(3a)–Ga(1a)–I(4) 110.8(1). Symmetry transformations used to generate equivalent atoms: ': -x + 2, -y + 2, -z + 1.

of 7 i.e.  $[(\eta^5-C_5H_5)Ru(GaI_4)(\mu-dppe)]_2$  (8, Fig. 5). Intriguingly the molecular structure of 8 reveals not only bridging (rather than chelating) dppe ligands, but also an  $\eta^1$ -coordinated  $[GaI_4]^-$  moiety with Ru–I [2.714(10) Å] and Ga–I [2.612(9) Å] contacts for the bridging unit which are closely reminiscent of those found for 5. The origins of 8 are not entirely clear - it could be that a mixture of products is formed in the reaction of  $(\eta^5-C_5H_5)Ru(dppe)Cl$  (6) with excess 'GaI,' or that the starting material 6 is contaminated with a trace of  $[(\eta^5-C_5H_5)RuCl(\mu-dppe)]_2$ . This dimeric species is known to be a minor product formed in the synthesis of 6 from  $(\eta^5-C_5H_5)Ru(PPh_3)_2Cl$  and dppe (as was employed herein) [19], although no trace was detected in the <sup>31</sup>P NMR spectrum of the starting material. Conceivably however, given the minute amounts of 8 which are formed, the presence of a trace quantity of  $[(\eta^5-C_5H_5) RuCl(\mu-dppe)$  impurity cannot be ruled out. Finally, the structures determined crystallographically for the isomeric species 7 and 8 point to a relatively small energetic difference between coordinating and non-coordinating modes of the  $[GaI_4]^-$  anion.

### 4. Conclusions

In conclusion, it has been shown that insertion of 'GaI' into the metal halogen bond of a half-sandwich metal carbonyl complex is a viable synthetic route for the generation of Mo–Ga bonds. However, in the case of  $[(\eta^7-C_7H_7)M_9-G_7H_7)M_9$  $(CO)_2GaI_2_2$  (2) it was found that further reaction of this complex with dppe does not proceed via the desired carbonyl ligand substitution process, instead forming  $[(\eta^7 C_7H_7$ )Mo(CO)<sub>2</sub>GaI<sub>2</sub>)<sub>2</sub>(u-dppe) (3). The isolation of 3 is rationalized by the Lewis acidity of the diiodogallyl centres and its very low solubility, which mitigates against further reaction in solution (as has been observed for related iron systems). By contrast, attempted 'GaI' insertions involving the metal-halogen bonds of complexes bearing ancillary phosphine ligands do not yield Ru-Ga containing products. Instead complexes containing the tetraiodogallate(III) anion/ligand are isolated. The compound formulated as 'GaI' is known to undergo disproportionation reactions in the presence of phosphine donors [8b], and a possible explanation for the formation of Ga(III) species from the reactions of  $(\eta^5-C_5H_5)Ru(PPh_3)_2Cl$  and  $(\eta^5-C_5H_5)Ru(dp$ pe)Cl with 'GaI' involves disproportionation to Ga(III) and gallium metal mediated by reversible dissociation of the ruthenium-bound phosphine ligands.

#### Appendix A. Supplementary material

CCDC 634453, 634454, 634455, 634456 and 634457 contain the supplementary crystallographic data for **2**, **3**, **5**, **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.02.037.

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