Structures of the Metallated Trihalogallate and Indate Ions $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2Br]^-$

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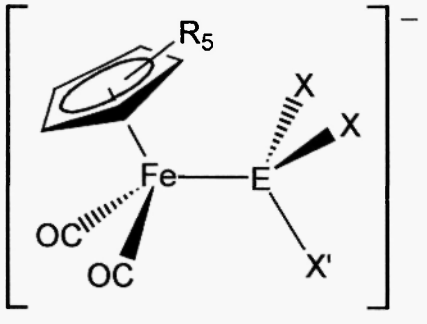
ABSTRACT

The metallated trihalogallate and indate ions $[(\eta^5\text{-}C_5R_5)Fe(CO)_2E(X)_2X']^-$ (**1**: R = Me, E = In, X = X' = I; **2**: R = H, E = Ga, X = I, X' = Br) isolated as the $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_5Me)]^+$ and $[Et_3NH]^+$ salts, respectively, each features a staggered conformation about the Fe-E bond [∠ centroid-Fe-E-X' = 178.9(3) (for **1**) and 176.6(10)° (for **2**)]. **1** represents the first crystallographically characterized half-sandwich iron complex containing a pendant trihaloindate fragment.



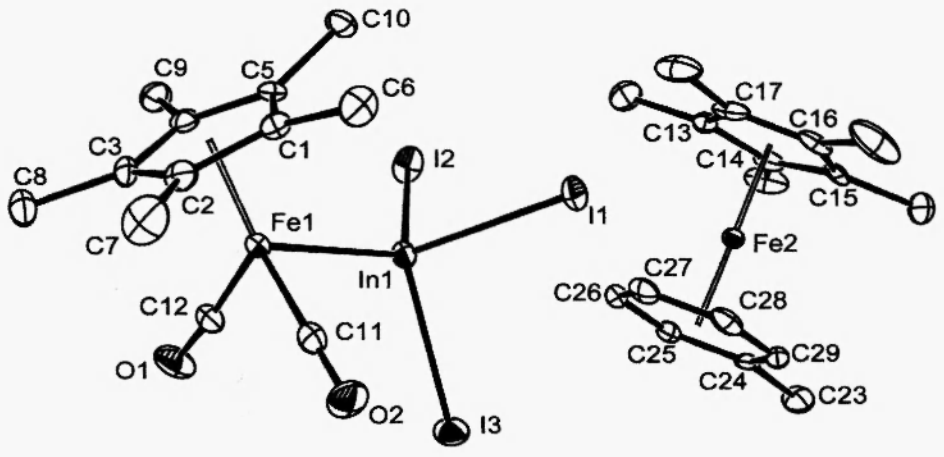


Fig. 1: Molecular structure of $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_5Me)]^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$, **1** (hydrogen atoms omitted for clarity, 30% ellipsoids). Key geometric parameters (Å, °): Fe(1)-In(1) 2.528(1), Fe(1)-C_5Me_5 centroid 1.723(5), Fe(1)-C(11) 1.749(7), In(1)-I(1) 2.794(1), In(1)-I(2) 2.805(1), In(1)-I(3) 2.806(1), C_5Me_5 centroid-Fe(1)-In(1)-I(3) 178.9(3).

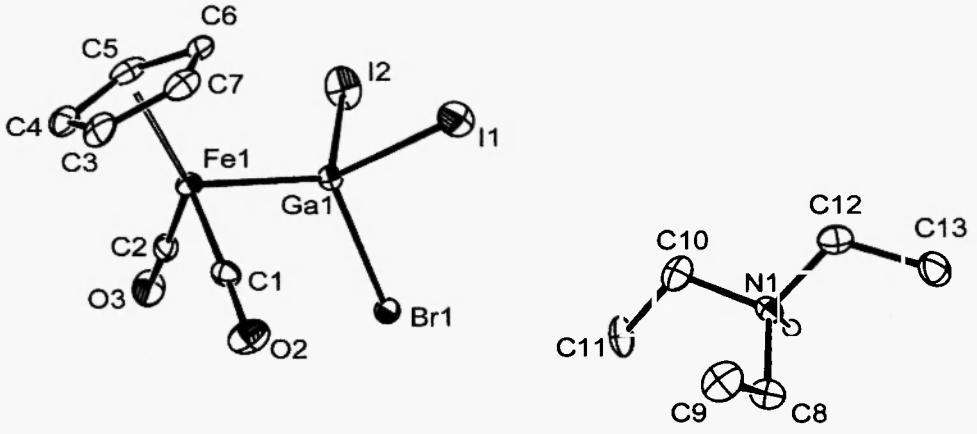


Fig. 2: Molecular structure of $[Et_3NH]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2Br]^-$, **2** (hydrogen atoms apart from that attached to N(1) omitted for clarity, 30% ellipsoids). Key geometric parameters (Å, °): Fe(1)-Ga(1) 2.338(2), Fe(1)-C_5H_5 centroid 1.717(11), Fe(1)-C(1) 1.742(12), Ga(1)-I(1) 2.544(2), Ga(1)-I(2) 2.527(2), Ga(1)-Br(1) 2.443(2), C_5H_5 centroid-Fe(1)-Ga(1)-Br(1) 176.6(10).

COMMENT

$[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_5Me)]^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$, **1** is isolated as a minor product from the reaction of InI with either $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ or $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$ /I/ in a manner similar to the synthesis of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_5Me)]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_3]^-$, reported by Linti and co-workers /2/. **2** is isolated from the 1:1 reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Ga(I)Br]_2$ /3/ with trimethylamine in toluene. The origins of the proton of the $[Et_3NH]^+$ cation are not immediately clear, but its location from X-ray diffraction data is supported by the results of ^1H NMR spectroscopy and mass spectrometry; in addition a number of related salts of the type $[BaseH]^+[(\eta^5\text{-}C_5R_5)Fe(CO)_2EX_3]^-$ have been reported from similar reaction chemistry /3/ The geometries of both anions (Figures 1 and 2) feature a staggered conformation about the Fe-E bond [$\angle$ centroid-Fe(1)-In(1)-I(3) = 178.9(3) (for **1**) and $\angle$ centroid-Fe(1)-Ga(1)-Br(1) = 176.6(10)° (for **2**)], presumably on steric grounds. A similar geometry is found for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_3]^-$, which is the only other previously reported half-sandwich iron complex containing a pendant trihalogallate or –indate fragment /2/. The Fe-Ga bond length in **2** [2.338(2) Å] is marginally shorter than that found in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_3]^-$ [2.361(7) Å], falling within the range of bond lengths expected for four-coordinate halogallyl/halogallate species bound to an $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ fragment (2.286 – 2.436 Å) /4/. Likewise the Fe-In distance in 1 [2.528(1)] is consistent with that found for other examples of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ species bound to four-coordinate indium-based ligands {e.g. 2.553(1) Å for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_4In_2(\mu\text{-}Cl)_2$} /5/.

EXPERIMENTAL

Preparation of $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_5Me)]^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$, 1

1 was isolated in 25 % yield from the 1:1 reaction of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2I$ (408 mg, 1.09 mmol) and InI in refluxing toluene (48 h) after filtration while hot and subsequent crystallization at –30°C. Salient spectroscopic data: ^1H NMR (CD_2Cl_2), δ 1.83 (15H, C_5Me_5), 1.88 (15H, C_5Me_5), 2.32 (3H, CH_3 of C_6H_5Me), 5.31 (2H, C_6H_5Me), 5.57 (1H, C_6H_5Me), 5.75 (2H, C_6H_5Me). ^{13}C NMR (CD_2Cl_2) δ 10.0, 10.3 (CH_3 of C_5Me_5), 18.1 (CH_3 of C_6H_5Me), 77.1, 88.7 (quaternary of C_5Me_5), 89.4, 90.9, 94.4 (C_6H_5Me), 216.0 (CO). IR (dichloromethane solution, cm^{-1}), 2001, 1970, 1947, 1922. Mass spec. (EI), 743.1 (3 %) $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^+$.

Preparation of $[Et_3NH]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2Br]^-$, 2

2 was prepared from the 1:1 reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Ga(I)Br]_2$ (125 mg, 0.14 mmol) /3/ and trimethylamine in toluene over 12 h at 20°C. Removal of volatiles *in vacuo*, and recrystallization from dichloromethane/hexane (ca. 1:2) at –30°C, led to the isolation of **2** as pale yellow crystals (38 %). Salient spectroscopic data: ^1H NMR (CD_2Cl_2), δ 1.33 (9H, CH_3 of Et_3NH^+), 3.26 (6H, CH_2 of Et_3NH^+), 4.74 (5H, $\eta^5\text{-}C_5H_5$), 7.20 (1H, NH of Et_3NH^+). ^{13}C NMR (CD_2Cl_2) δ 9.8 (CH_3 of Et_3NH^+), 48.3 (CH_2 of Et_3NH^+) 84.0 (C_5H_5), CO resonance not observed. IR (dichloromethane solution, cm^{-1}), ν(CO) 1995, 1944. Mass spec.

(ES+), 102.1 (100 %) $[Et_3NH]^+$; (CI) 499.7 (5 %) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2]^+$, 451.7 (8 %) $[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaIBr]^+$.

CRYSTALLOGRAPHY

Table 1

$[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_5Me)]^+[(\eta^5\text{-}C_5Me_5)Fe(CO)_2InI_3]^-$ (**1**) and $[Et_3NH]^+[(\eta^5\text{-}C_5H_5)Fe(CO)_2GaI_2Br]^-$ (**2**)

	1	**2**
Formula	$C_{29}H_{38}Fe_2I_3InO_2$	$C_{13}H_{21}BrFeGaI_2NO_2$
Formula weight	1025.81	682.59
Crystal system	Monoclinic	Monoclinic
Crystal size, mm	0.25 x 0.10 x 0.05	0.35 x 0.20 x 0.18
Space group	$P2_1/c$	$P2_1/c$
***a*, Å**	13.1823(2)	12.7451(5)
***b*, Å**	13.3528(3)	11.9869(5)
***c*, Å**	19.5415(5)	13.1591(6)
β, °	102.149(1)	93.417(2)
***V*, Å^3**	3362.67(13)	2006.80(15)
Z	4	4
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD
Temperature, K	150(2)	150(2)
μ(Mo-K$_\alpha$), mm^{-1}	4.309	7.135
***D*$_{calcd}$, g cm^{-3}**	2.026	2.259
***F*(000)**	1952	1280
ϑ_{max}, °	27.49	27.49
Reflections measured	35496	13364
Unique reflections	7673	4584
***R*(F^2), *R*$_w$(F^2) (*I* > 2σ(*I*))**	0.0482, 0.0967	0.0778, 0.2139
ρ, eÅ^{-3}	1.140	2.345
G.O.F.	1.029	1.060
No. observables/parameters	7673 / 345	4584 / 193
Programs used	SHELX-97 [6]	SHELX-97 [6]
CCDC deposition number	271189	271190

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the EPSRC.

REFERENCES

1. For earlier reports of In(I) halide insertion chemistry see: A.T.T. Hsieh and M.J. Mays, *J. Organomet. Chem.* (1972) *37* 9.
2. G. Linti, G. Li and H. Pritzkow, *J. Organomet. Chem.* (2001) *626* 82.
3. N. R. Bunn, S. Aldridge, D.L. Kays, N.D. Coombs, J.K. Day, L.-L. Ooi, S.J. Coles and M.B. Hursthouse, *Organometallics* (2005) submitted.
4. As determined by a survey of the Cambridge Structural Database.
5. L.M. Clarkson, N.C. Norman and L.J. Farrugia, *Organometallics* (1991) *10* 1286.
6. G.M. Sheldrick, *SHELX-97*, University of Göttingen, Germany (1997).