Reactivity of Ir(III) carbonyl complexes with water; alternative by-product formation pathways in catalytic methanol carbonylation

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Supplementary Information

Kinetic data

Figure S1: Plot of absorbance versus time for the 2342 cm^{-1} band of CO_2 in the reaction of $[Ir(COMe)(CO)_2I_3]^-$ with water (0.56 mol dm^{-3}) in acetonitrile at 42 °C.

Table S1. Observed rate constants (k_{obs}) for reactions of $[Ir(CO)_2I_3(COMe)]^-$ with water in MeCN 42 °C.

Figure S2: Plot of absorbance versus time for the 2157 cm^{-1} ν(CO) band of $[Ir(CO)_3I_2Me]$ during reaction with water (0.694 mol dm^{-3}), under 20 bar CO, in CH_2Cl_2/THF(3:1, v/v) at 23 ºC.

Table S2. Observed rate constants (k_{obs}) for reactions of $[Ir(CO)_3I_2Me]$ with H_2O or D_2O under 20 bar CO, in CH_2Cl_2/THF(3:1, v/v) at 23 ºC. Calculate kinetic isotope effect (k_H/k_D) values are also given.

Computational data

Table S3 Cartesian coordinates for DFT-optimised structures

Table S4. Computed relative energies (in kJ mol^{-1}) for optimised structures and transition states from DFT calculations.

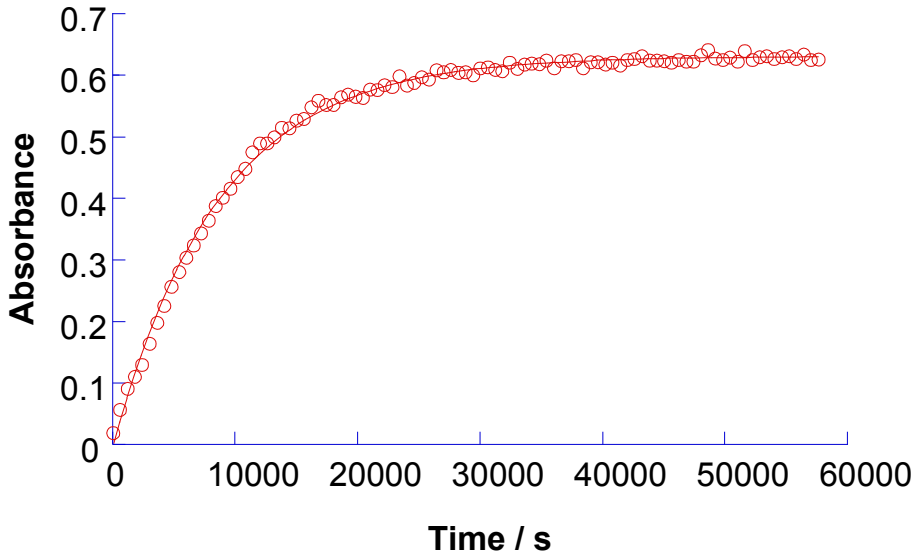

Figure S1: Plot of absorbance versus time for the 2342 cm^{-1} band of CO_2 in the reaction of $[Ir(COMe)(CO)_2I_3]^-$ with water (0.56 mol dm^{-3}) in acetonitrile at 42 °C.

Table S1. Observed rate constants (k_{obs}) for reactions of $[Ir(CO)_2I_3(COMe)]^-$ with water in MeCN 42 °C.

$[H_2O]$ / mol dm^{-3}	10^4 k_{obs} / s^{-1}
0.56	0.994
1.11	1.54
1.67	2.04
2.78	3.57
0.56[a]	2.12

a) in the presence of Bu_4NI (0.15 mol dm^{-3})

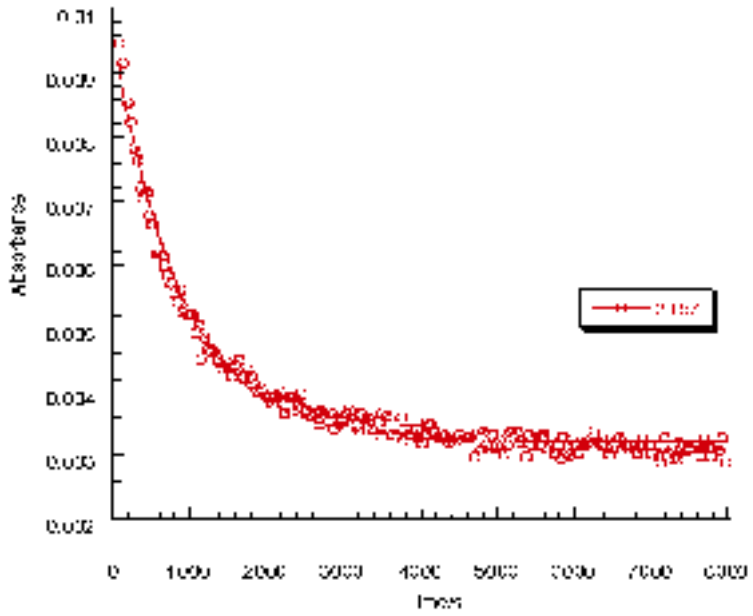

Figure S2: Plot of absorbance versus time for the 2157 cm^{-1} ν(CO) band of $[Ir(CO)_3I_2Me]$ during reaction with water (0.694 mol dm^{-3}), under 20 bar CO, in CH_2Cl_2/THF(3:1, v/v) at 23 ºC.

Table S2. Observed rate constants (k_{obs}) for reactions of $[Ir(CO)_3I_2Me]$ with H_2O or D_2O under 20 bar CO, in CH_2Cl_2/THF(3:1, v/v) at 23 ºC. Calculate kinetic isotope effect (k_H/k_D) values are also given.

$[H_2O]$ / mol dm^{-3}	10^3 k_{obs} / s^{-1} (H_2O)	10^3 k_{obs} / s^{-1} (D_2O)	k_H/k_D
0.35	0.798	0.648	1.23
0.69	1.13	0.821	1.38
1.04	1.55	1.16	1.34
2.08	2.30	-	-

Table S3. Cartesian coordinates for DFT-optimised structures.

Gas Phase

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(conformer 1)

Ir	0.13073322	0.60721552	-0.02538115
C	0.20576973	0.66206145	-2.18100429
H	0.99263263	-0.01013200	-2.52360439
H	-0.75147992	0.31088489	-2.56686926
H	0.40883315	1.66112685	-2.57551789
I	1.49489403	-1.89147067	-0.07777087
I	-2.51392937	-0.70519996	-0.06872652
C	-0.84161913	2.20322800	-0.14072765
O	-1.43222690	3.17626953	-0.23232353
C	0.11714155	0.40188631	1.95121956
O	0.10297769	0.29620913	3.08440042
C	1.90663123	1.72238696	-0.07087996
O	1.96666348	2.87310243	0.28142554
O	3.01782227	1.12482965	-0.56251526
H	2.82505322	0.18216485	-0.71147162

Energy : -583.35829737 a.u.

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(conformer 2)

Ir	0.13846725	0.58227080	-0.04213221
C	0.06022898	0.60803056	-2.19413519
H	-0.21602398	-0.39892092	-2.50305390
H	-0.68309504	1.30612504	-2.58715343
H	1.04372287	0.87269169	-2.57800484
I	1.62376714	-1.81411064	-0.24273317
I	-2.45299411	-0.75931859	-0.02732011
C	-0.82046884	2.18671274	-0.09966789
O	-1.39284420	3.17727184	-0.15884733
C	0.21626513	0.29783076	1.93461215
O	0.21654935	0.11891423	3.05789256
C	1.95904696	1.57906175	-0.12358556
O	2.53037500	2.03529549	-1.08036780
O	2.51355052	1.74480689	1.12835264
H	3.36088228	2.19271350	0.97010416

Energy : -583.35231813 a.u.

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(isomer, Me trans to CO_2H)

Ir	-0.00000653	0.64174706	-0.20768352
I	-2.06303501	-1.28748274	-0.02578164
C	1.40629649	1.87290502	-0.38511387
O	2.23956323	2.64389110	-0.52271491
C	-1.40584290	1.87327731	-0.38617846
O	-2.23886132	2.64440393	-0.52444035
C	-0.00079104	0.91056222	1.96723104
O	-0.00135505	1.99198163	2.50596452
O	0.00034847	-0.19902667	2.76230097
H	0.00122815	-0.97564757	2.18564510
C	0.00069177	0.24840827	-2.39338350
H	0.88996321	0.65878254	-2.87755156
H	-0.00129455	-0.83289659	-2.51473093
H	-0.88621861	0.66221339	-2.87898803
I	2.06214380	-1.28833461	-0.02491774

Energy : -583.33993703 a.u.

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(TS for H transfer to Me)

Ir	0.20031700	0.56753802	-0.00203800
C	0.28935501	0.58880597	-2.37529302
H	0.98458499	-0.01027500	-2.97201705
H	-0.57195997	-0.06235300	-2.20917010
H	-0.05724600	1.46175098	-2.93159890
I	1.52434194	-1.87070501	-0.06001900
I	-2.65829396	-0.61253798	-0.08945100
C	-0.69482899	2.23541188	-0.03556900
O	-1.23926198	3.23972011	-0.04858600
C	0.12138200	0.36274001	1.87139797
O	0.08326200	0.25306901	3.00474095
C	2.15162110	1.57397902	-0.03370400
O	2.70259309	1.90016305	0.98232502
O	2.42613792	1.71224594	-1.26583600
H	1.33266699	1.11510396	-1.75051105

Energy : -583.30812172 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(conformer 1)

Ir	0.22474380	0.63125849	-0.06083686
C	0.20244394	0.62489533	-2.19081163
H	0.99928039	-0.00051428	-2.59181499
H	-0.75374591	0.17258649	-2.48197126
H	0.26442349	1.61495769	-2.64546204
I	1.28711152	-1.90492213	-0.12884606
C	-0.77074927	2.24289274	-0.17896844
O	-1.39995646	3.18508005	-0.27823234
C	0.17109364	0.43540117	1.94311309
O	0.11571227	0.31287104	3.06770182
C	1.95244384	1.77785325	0.01352414
O	1.98070025	2.87660193	0.46286228
O	3.01460028	1.16213000	-0.50678843
H	2.80396008	0.24175729	-0.73887944

Energy : -571.77750973 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(conformer 2)

Ir	0.25682420	0.53882092	-0.07408620
C	0.09058560	0.68406439	-2.19521236
H	0.86961132	0.07108460	-2.64380121
H	-0.88604420	0.27653873	-2.47711253
H	0.16870439	1.70210767	-2.57960510
I	0.71720088	-2.12982631	-0.37708446
C	-0.54939103	2.24443555	-0.01072109
O	-1.08574569	3.25019360	-0.00139815
C	0.32323614	0.17706104	1.91162288
O	0.31687012	-0.03588980	3.02434158
C	2.08679533	1.42271221	-0.04814488
O	2.96490383	1.07847917	-0.77510798
O	2.20104480	2.39869094	0.88265848
H	3.11227846	2.73340130	0.83177179

Energy : -571.77460912 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(TS for H transfer to Me)

Ir	0.53143626	0.05532664	-0.29842865
C	0.48904064	-2.18040371	-0.88150686
H	-0.25541636	-2.89585018	-0.51248938
H	0.07461784	-1.84913707	-1.83651245
H	1.43410242	-2.68731952	-1.07913077
I	-2.15646338	-0.05969784	0.02976203
C	2.37756109	0.09026870	-0.73157179
O	3.47839308	0.11764606	-1.02760696
C	0.40117648	1.92993212	0.04071690
O	0.32895583	3.04556847	0.24144632
C	0.99706101	-0.54767406	1.84237337
O	1.22644424	0.28556114	2.63960290
O	0.89557976	-1.79043198	1.71695507
H	0.65209210	-1.90382373	0.48967934

Energy : -571.74103156 a.u.

$[Ir(CO)_2I_2HMe]^-$

Ir	-0.05148416	0.81505215	-0.07690963
C	-0.02571186	0.69985694	-2.23139095
H	0.08377764	-0.35530540	-2.48004150
H	-0.93949836	1.07262588	-2.70164108
H	0.82617807	1.25368667	-2.62969542
I	2.38417339	-0.62586701	-0.10305273
I	-1.82196057	-1.53653181	0.05960163
C	-1.55734074	1.89272988	-0.24481094
O	-2.46566248	2.58325672	-0.37216210
C	0.11994410	0.81977558	1.88650513
O	0.22421946	0.85088408	3.02248573
H	0.90874851	2.05928636	-0.25666305

Energy : -394.72619070 a.u.

$[Ir(CO)_2I_2HMe]^-$
(TS for Me-H elimination)

Ir	0.01470363	0.79740870	-0.16967620
C	0.05256208	0.45870057	-2.45730162
H	-0.37209547	-0.53831023	-2.35955524
H	-0.62557894	1.10315919	-3.01529074
H	1.01135898	0.37633634	-2.97010279
I	2.31717443	-0.82089263	-0.04625266
I	-2.01984549	-1.42642713	0.27639216
C	-1.46894586	1.91615713	-0.30205753
O	-2.37297082	2.61877370	-0.40291548
C	0.48964754	1.38381398	1.57746983
O	0.78802627	1.78189456	2.61312246
H	0.67966759	1.42006671	-1.52789521

Energy : -394.69050848 a.u.

MeCN (PCM solvation model)

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(conformer 1)

Ir	0.13045992	0.60544807	-0.01910373
C	0.24594720	0.65673816	-2.17162466
H	1.05777240	0.00960141	-2.50490284
H	-0.69296324	0.28264540	-2.58099103
H	0.42437497	1.66047013	-2.56380796
I	1.53076553	-1.86866617	-0.02913213
I	-2.47883439	-0.78968406	-0.11760417
C	-0.86508930	2.19090056	-0.15334287
O	-1.47061908	3.15097213	-0.25528377
C	0.08347663	0.42599922	1.97172987
O	0.05304630	0.32755587	3.10216761
C	1.88025331	1.73663497	-0.02999163
O	1.93802524	2.87124205	0.37884155
O	2.99453664	1.18561769	-0.56422836
H	2.82624602	0.25095758	-0.77342111

Energy : -583.42323325 a.u.

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(conformer 2)

Ir	0.14064379	0.51901567	-0.05139900
C	0.08265071	0.57161164	-2.20100546
H	-0.36441529	-0.36510348	-2.53322506
H	-0.50992268	1.39684045	-2.60263896
H	1.10173559	0.64940810	-2.57779360
I	1.38567233	-2.02091837	-0.23010649
I	-2.54862285	-0.66644537	-0.05197575
C	-0.70556134	2.19178820	-0.07208200
O	-1.22068286	3.20949459	-0.10688151
C	0.21589692	0.27129281	1.93359005
O	0.24088316	0.12084313	3.05859041
C	2.00542784	1.41982782	-0.12554415
O	2.86074376	1.28436315	-0.96278268
O	2.19801331	2.26489520	0.93095958
H	3.08271170	2.65608740	0.82482249

Energy : -583.42280768 a.u.

$[Ir(CO)_2I_2(CO_2H)Me]^-$
(TS for H transfer to Me)

Ir	0.22387621	0.59347630	0.00077305
C	0.29843482	0.63088822	-2.36284471
H	0.98931438	0.06477065	-2.99808955
H	-0.55431157	-0.03647349	-2.23101902
H	-0.04819823	1.52907598	-2.87396431
I	1.47276831	-1.89072704	-0.04997140
I	-2.62717175	-0.58881372	-0.08096984
C	-0.61501306	2.29988599	-0.04511450
O	-1.13157988	3.31309128	-0.07047483
C	0.12453978	0.41490939	1.88598490
O	0.08045553	0.31130427	3.01708460
C	2.18876934	1.48779964	-0.01584925
O	2.77299213	1.77703297	0.99916875
O	2.50208926	1.61154580	-1.24457932
H	1.37977982	1.08355188	-1.74220061

Energy : -583.37618762 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(conformer 1)

Ir	0.53751111	0.05018428	-0.35086015
C	0.47429752	-1.96497846	-1.04309118
H	-0.33470890	-2.51889086	-0.56709033
H	0.25477344	-1.88847005	-2.11475778
H	1.40635645	-2.51650882	-0.91696364
I	-2.23558450	-0.01667494	-0.05258269
C	2.38563919	0.04212515	-0.78738546
O	3.48529935	0.02162628	-1.07267058
C	0.43561232	1.97416806	0.25882560
O	0.38061741	3.04201674	0.63013262
C	1.07258987	-0.60445875	1.51670599
O	2.13256240	-0.36647245	2.01981306
O	0.15842967	-1.35361671	2.14761090
H	-0.66870755	-1.39735854	1.63934147

Energy : -571.79490421 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(conformer 2)

Ir	0.48020026	-0.09898656	-0.33579025
C	0.35637736	-2.22731495	-0.40908840
H	-0.29891521	-2.57549453	0.38762653
H	-0.09299290	-2.47312355	-1.37763846
H	1.31768358	-2.73670697	-0.32976234
I	-2.23262763	-0.04073130	0.23449093
C	2.26302814	-0.27190268	-0.95677823
O	3.32384634	-0.39827707	-1.34726584
C	0.39867824	1.92138445	-0.33626410
O	0.34127626	3.05207181	-0.34739712
C	1.19772184	-0.11755324	1.56086373
O	0.72124827	-0.77266043	2.44158149
O	2.26427674	0.69371581	1.71406412
H	2.55638456	0.63812399	2.64043593

Energy : -571.79447506 a.u.

$[Ir(CO)_2I(CO_2H)Me]$
(TS for H transfer to Me)

Ir	0.55208099	0.03213900	-0.31962100
C	0.51729101	-2.22793508	-0.86448300
H	-0.30071101	-2.90081310	-0.58715302
H	0.25452599	-1.87465203	-1.86542904
H	1.45692599	-2.77473211	-0.94777900
I	-2.18700910	-0.03391400	-0.07432200
C	2.43235111	0.03353100	-0.62525398
O	3.55076003	0.04212300	-0.82595903
C	0.45510599	1.91541505	-0.00063100
O	0.39807501	3.03037190	0.20295200
C	0.85036302	-0.48721501	1.77302301
O	1.02991295	0.34893700	2.60031605
O	0.75356197	-1.74793696	1.74530196
H	0.60139698	-1.91783094	0.47338301

Energy : -571.75520498 a.u.

Table S4. Computed relative energies (in kJ mol^{-1}) for optimised structures and transition states from DFT calculations.
E = electronic energy, *E*(RB+HF-LYP); *H* = sum of electronic and thermal enthalpies; *G* = sum of electronic and thermal free energies.

	Gas phase			MeCN (PCM solvation model)		
Complex	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
$[Ir(CO)_2I_2(CO_2H)Me]^-$ (conformer 1)	0.00	0.00	0.00	0.00	0.00	0.00
$[Ir(CO)_2I_2(CO_2H)Me]^-$ (conformer 2)	15.70	15.47	13.37	1.12	1.00	-0.41
$[Ir(CO)_2I_2(CO_2H)Me]^-$ (isomer, Me trans to CO_2H)	48.21	47.46	46.88	-	-	-
$[Ir(CO)_2I_2(CO_2H)Me]^-$ (TS for H transfer to Me)	131.74	114.62	117.88	123.52	106.40	109.49
$[Ir(CO)_2I(CO_2H)Me]$ (conformer 1)	0.00	0.00	0.00	0.00	0.00	0.00
$[Ir(CO)_2I(CO_2H)Me]$ (conformer 2)	7.62	7.93	7.03	1.13	1.26	0.50
$[Ir(CO)_2I(CO_2H)Me]$ (TS for H transfer to Me)	95.77	79.45	83.06	104.23	88.29	91.78
$[Ir(CO)_2I_2HMe]^-$	0.00	0.00	0.00	-	-	-
$[Ir(CO)_2I_2HMe]^-$ (TS for Me-H elimination)	93.68	88.41	87.63	-	-	-