Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Nickel-catalyzed Release of H_2 from Formic Acid and a New Method for the Synthesis of Zerovalent $Ni(PMe_3)_4$

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Table 1. Cartesian Coordinates for Geometry Optimized $Ni(PMe_3)_4$

$Ni(PMe_3)_4$

E^{SCF} = -2014.12566831303 Hartrees

G = -2013.444168 Hartrees

atom	x	y	z
Ni	4.711899941	6.824485091	4.525779837
P	5.214013594	6.657470757	2.369256262
P	3.593485289	5.017173745	5.166839971
P	6.582110585	6.99972671	5.708395907
P	3.4576734	8.628405382	4.853988979
C	6.450645711	7.847865882	1.632858566
C	3.852852727	6.856328491	1.10576611
H	3.064728282	6.122108814	1.298232276
H	4.215843142	6.727970729	0.078129305
H	3.410202635	7.853023111	1.199320581
C	5.95208793	5.064156257	1.732234294
H	5.252400454	4.24101797	1.90825268
H	6.872471641	4.842206923	2.280850262
H	6.179131348	5.109419401	0.65954973
C	2.171844374	4.412012609	4.1173097
C	2.729587515	5.029624604	6.822875787
H	1.980235493	5.827337041	6.838162688
H	3.456555522	5.240156228	7.613134577
H	2.232428974	4.075975858	7.041231367
C	4.512287564	3.40074631	5.345649851
H	5.300072297	3.509424586	6.097764057
H	4.991638128	3.145296757	4.395734318
H	3.852212511	2.576467996	5.644213717

C	6.502387262	6.805935869	7.564455353
C	7.983172714	5.812763282	5.366591672
H	7.631064479	4.78472121	5.494888343
H	8.842355826	5.980175794	6.028416874
H	8.312752806	5.925199094	4.328884666
C	7.548897415	8.596353019	5.638424132
H	6.925135551	9.417692611	6.005053942
H	7.815146832	8.817545619	4.600432302
H	8.465635383	8.555431299	6.240232192
C	3.982830822	10.24699412	4.083934541
C	3.176851663	9.230342809	6.599570474
H	2.729207767	8.42916749	7.195396107
H	2.522190242	10.11026136	6.636723802
H	4.137640094	9.488450156	7.056065298
C	1.681109398	8.611956114	4.277799951
H	1.137527147	7.813031741	4.791926852
H	1.646333333	8.401554613	3.204570629
H	1.171548834	9.564507391	4.470709543
H	2.53843553	4.156449725	3.118036548
H	1.432206041	5.210825575	4.006821442
H	1.681617859	3.529748527	4.54819985
H	7.414347173	7.732998954	2.139064992
H	6.11020073	8.875394726	1.793053953
H	6.596862429	7.684793194	0.557492043
H	6.125532962	5.808445157	7.811869139
H	5.803595596	7.538651113	7.979471633
H	7.48240141	6.939468681	8.039955832
H	4.01388573	10.14060368	2.994925146

H	4.991185716	10.50370729	4.422578675
H	3.301914234	11.06950143	4.337297018

Table 2. Cartesian Coordinates for Geometry Optimized *trans*-$Ni(PMe_3)_2(O_2CH)_2$

trans-$Ni(PMe_3)_2(O_2CH)_2$

E^{SCF} = -1470.27597168716 Hartrees

G = -1469.761944 Hatrees

atom	x	y	z
Ni	0.960817883	2.137505747	2.894405973
P	2.601576578	1.907880985	4.486514493
P	-0.6338954	2.368555903	1.255507643
O	0.899253072	4.025177125	2.97938386
O	0.920251631	0.247323494	2.904996829
C	2.191283417	0.596605713	5.715430623
C	3.068787828	3.335159978	5.553061648
C	4.194303279	1.362650742	3.748078472
C	-1.904002542	3.628145653	1.700618212
C	0.090834862	2.985360272	-0.317234474
C	-1.654299728	0.923765667	0.741857318
H	3.046578917	0.39029728	6.36784437
H	1.89782732	-0.31036535	5.183578828
H	1.346472041	0.923488149	6.329438338
H	3.763167377	3.012136256	6.336135164
H	2.173740097	3.755829132	6.019728025
H	3.542594969	4.103402897	4.939816907
H	4.53595726	2.144021254	3.065177061
H	4.037450975	0.442810524	3.178872156
H	4.947499177	1.185009573	4.523421817

H	-2.559532876	3.84086771	0.849276166
H	-1.400523914	4.54125883	2.0236404
H	-2.510561319	3.257281323	2.532524786
H	-0.688109031	3.161395052	-1.067119834
H	0.798939386	2.237136244	-0.680929906
H	0.629859851	3.917691014	-0.13023179
H	-2.445374033	1.243016479	0.054844858
H	-2.109708569	0.461635079	1.622139514
H	-1.016281167	0.18996596	0.246742478
C	1.962838411	4.717561166	2.697118246
H	1.764514011	5.808196816	2.709557481
O	3.089414794	4.289308487	2.44903831
C	1.228516901	-0.407500753	1.825086266
H	1.234410535	-1.503598993	1.990630573
O	1.481943487	0.059048051	0.714932395

Table 3. Cartesian Coordinates for Geometry Optimized *cis*-$Ni(PMe_3)_2(O_2CH)_2$

cis-$Ni(PMe_3)_2(O_2CH)_2$

E^{SCF} = -1470.25965153444 Hartrees

atom	**x**	**y**	**z**
Ni	0.825271297	2.831769702	0.284442542
P	2.186214051	2.925511146	2.096515716
P	-0.975249306	1.894801803	1.298380921
C	1.452577464	3.485190333	3.701373492
C	3.021095613	1.338348789	2.513643529
C	3.58464712	4.107767653	1.922555923
C	-0.67771257	0.502140048	2.481420805
C	-2.164804601	1.112914384	0.133400996

C	-2.024161697	3.073826182	2.247126611
O	2.179759269	3.72825253	-0.719353696
O	-0.118563186	2.72939199	-1.372135784
H	3.210028892	5.080616652	1.596830385
H	4.281011028	3.733273795	1.17163955
H	4.102993149	4.210433858	2.881612577
H	3.55004567	1.007021147	1.616779836
H	2.289221559	0.577096739	2.794233768
H	3.725829994	1.478734979	3.340279936
H	0.664629483	2.810122391	4.041980406
H	1.022425646	4.483132264	3.575407966
H	2.226486749	3.531291931	4.474643984
H	-0.076599706	0.819691036	3.33607983
H	-0.147715414	-0.304529643	1.966431427
H	-1.63105817	0.113682474	2.854685926
H	-2.30502851	3.87807839	1.562802555
H	-1.468160603	3.500646113	3.085319798
H	-2.918808199	2.571374727	2.63029036
H	-1.634069258	0.439674991	-0.543295715
H	-2.651532472	1.888844734	-0.458238685
H	-2.920735516	0.55554044	0.69635325
C	-1.011372041	3.639851549	-1.579007103
O	-1.537874573	4.370865028	-0.731464425
H	-1.316955498	3.705301936	-2.641540102
C	3.170734083	3.002264584	-1.11900926
O	3.501602723	1.892156725	-0.685243954
H	3.765122966	3.491473676	-1.915253491

Table 4. Cartesian Coordinates for Geometry Optimized *trans*-$Ni(PMe_3)_2(O_2CH)H$

trans-$Ni(PMe_3)_2(O_2CH)H$

E^{SCF} = -1281.60503392687 Hartrees

G = -1281.169265 Hartrees

atom	x	y	z
Ni	0.677076157	2.439223411	3.378802222
P	2.105124889	2.143018724	5.054844537
P	-0.955663499	2.497346356	1.866837585
O	2.073395051	3.462011596	2.46392429
H	-0.309258913	1.70059565	4.156551651
C	1.536223663	1.419220988	6.652379051
C	2.93664278	3.707618245	5.563739753
C	3.515574863	1.052035484	4.580944235
C	-2.656743377	2.703470178	2.55741799
C	-0.897676645	3.81984869	0.581578493
C	-1.082795899	0.949307528	0.878786197
H	2.356903003	1.338593808	7.373550208
H	1.115812272	0.426122596	6.47086297
H	0.746639815	2.047526376	7.074235387
H	3.749168535	3.518360958	6.273737422
H	2.205930348	4.378237502	6.025356883
H	3.326648646	4.191445409	4.664985768
H	3.991622828	1.458705018	3.685225845
H	3.143278631	0.051068038	4.345364092
H	4.254002529	0.98144154	5.387295594
H	-3.411347262	2.711114841	1.763270287
H	-2.714916216	3.644683725	3.112327844

H	-2.868048185	1.887119728	3.252880631
H	-1.789702242	3.782588136	-0.05365459
H	-0.004902148	3.67387654	-0.0291757
H	-0.840046985	4.800450349	1.06278746
H	-1.903452941	1.009129654	0.155212967
H	-1.252533098	0.100788185	1.547588738
H	-0.133073159	0.808298961	0.357551838
C	2.45133493	3.14223895	1.272199619
H	3.284380996	3.772071792	0.894969174
O	1.987582012	2.25131846	0.549829093

Table 5. Cartesian Coordinates for Geometry Optimized *cis*-$Ni(PMe_3)_2(O_2CH)H$

cis-$Ni(PMe_3)_2(O_2CH)H$

E^{SCF} = -1281.58782575245 Hartrees

atom	**x**	**y**	**z**
Ni	0.806738726	2.605798782	0.402161551
P	2.187635823	2.968088386	2.036187881
P	-1.254356245	2.103462315	1.371370494
C	1.726848215	2.688956582	3.812254509
C	3.766385077	2.020763262	1.924069586
C	2.742229627	4.726871196	2.070319569
C	-1.357199234	0.812246346	2.699900458
C	-2.535483022	1.494172294	0.191868308
C	-2.095506252	3.552968708	2.147616694
H	2.084192774	2.982069479	-0.20851293
O	0.130449353	2.450849563	-1.391107483
H	1.877274236	5.3802693	2.215566828
H	3.195674442	4.978084871	1.108885997

H	3.463672935	4.898871359	2.876384817
H	4.249319796	2.243247785	0.969892691
H	3.552750356	0.948351575	1.953713476
H	4.441189219	2.274818984	2.748510946
H	1.516092124	1.629143549	3.980449916
H	0.832280654	3.265245693	4.064983261
H	2.540673196	2.99421139	4.479052434
H	-0.760651513	1.103795984	3.567946117
H	-0.965685322	-0.135957833	2.318175833
H	-2.392990325	0.659249024	3.02257715
H	-2.162321834	4.338656763	1.390484202
H	-1.506219484	3.92752699	2.990240451
H	-3.09785726	3.292054818	2.505125919
H	-2.154973731	0.626437533	-0.353176611
H	-2.756990241	2.284691366	-0.527281484
H	-3.451875016	1.219606255	0.725579213
C	-0.637564679	3.415660444	-1.761977002
O	-1.099183706	4.319561909	-1.049228061
H	-0.898606896	3.375539679	-2.839146552

Table 6. Cartesian Coordinates for Geometry Optimized $Ni(PMe_3)_3(O_2CH)H$

$Ni(PMe_3)_3(O_2CH)H$

E^{SCF} = -1742.79136104551 Hartrees

G = -1742.185226 Hartrees

atom	**x**	**y**	**z**
Ni	7.781402982	5.329914634	21.14290514
P	8.341141322	6.365748476	19.15382889
H	7.061182344	6.515170703	21.55414098

P	9.056655481	5.752739594	22.99613272
O	8.795048516	3.758732812	20.4792874
P	5.735117241	4.319469913	21.31458682
C	7.80890156	8.090895466	18.73851543
H	8.190044612	8.782492361	19.49596748
H	6.716302748	8.148731541	18.75259718
H	8.170003352	8.407168517	17.75289639
C	7.792317771	5.429174802	17.65230908
H	8.201202489	5.854403221	16.72802434
H	6.699586453	5.433710836	17.59198124
H	8.126970525	4.393315839	17.75633895
C	10.75992031	5.02850951	23.00270713
H	11.31174166	5.320109891	23.9038024
H	11.31076836	5.363053796	22.11929003
H	10.6776018	3.939817003	22.96761323
C	9.412813178	7.529813009	23.38824864
H	8.470648867	8.067863666	23.52799292
H	9.943641881	7.992356563	22.55045346
H	10.02214791	7.633038285	24.29369831
C	10.16731581	6.450438009	18.85249787
H	10.5827249	5.449286943	18.99719585
H	10.63160072	7.124418386	19.57904254
H	10.40303026	6.80130673	17.84073322
C	8.407458008	5.143873548	24.61793898
H	8.2651088	4.063014724	24.54079392
H	7.440833579	5.611121053	24.82802261
H	9.098278664	5.368027394	25.43938645
C	5.505317314	2.757773424	20.34812143

H	6.211200834	2.010296494	20.7173181
H	5.71508688	2.939526351	19.2903892
H	4.48424249	2.373046794	20.45251106
C	4.259385265	5.304032115	20.77455394
H	3.326615411	4.742007431	20.90040816
H	4.366426476	5.579495745	19.72084973
H	4.202847642	6.226538881	21.35974779
C	5.210057744	3.771009355	23.00166268
H	5.157692817	4.634352493	23.67153294
H	5.96419382	3.077534931	23.38236449
H	4.231691475	3.276427787	22.97959127
C	8.905921875	2.683503085	21.17846077
H	9.501638513	1.895041279	20.67073859
O	8.436285135	2.458028435	22.30296155

Table 7. Cartesian Coordinates for Geometry Optimized *trans*-$Ni(PMe_3)_2H_2$

trans-$Ni(PMe_3)_2H_2$

E^{SCF} = -1092.91475737547 Hartrees

G = -1092.551915 Hartrees

atom	**x**	**y**	**z**
Ni	0.672444301	2.077267976	3.456090586
P	2.17429077	1.843087229	5.010055505
P	-0.828413835	2.315184625	1.902125905
H	0.718364826	3.600689413	3.522997628
H	0.62536452	0.55371302	3.389354324
C	1.604268957	0.891165203	6.488177789
C	2.915104606	3.349570391	5.786657711
C	3.676676881	0.902816898	4.4859304

C	-2.336617575	3.242817904	2.431930852
C	-0.260813945	3.280074384	0.431527521
C	-1.560726959	0.810578133	1.113867697
H	2.404808748	0.780025634	7.228296286
H	1.261787457	-0.094992034	6.165018339
H	0.759864157	1.40922092	6.95227368
H	3.657227617	3.097910884	6.553205861
H	2.116380657	3.947900851	6.23378987
H	3.385712007	3.95611809	5.007855983
H	4.165085229	1.426921028	3.659188622
H	3.370523062	-0.083659938	4.129107847
H	4.390805046	0.792707491	5.309895185
H	-3.04953812	3.357072846	1.607513434
H	-2.037253322	4.227385462	2.799528448
H	-2.823755525	2.70716722	3.252048804
H	-1.060148026	3.39235759	-0.309708207
H	0.586904755	2.768624019	-0.033902993
H	0.076641461	4.265526801	0.761891957
H	-2.302677762	1.063591296	0.347613309
H	-2.029645765	0.196712594	1.887931338
H	-0.758372452	0.218980645	0.664258275

Table 8. Cartesian Coordinates for Geometry Optimized *cis*-$Ni(PMe_3)_2H_2$

cis-$Ni(PMe_3)_2H_2$

E^{SCF} = -1092.91121713544 Hartrees

atom	**x**	**y**	**z**
Ni	0.783132464	2.708596177	0.462218396
P	2.398493699	2.786758475	1.991179402

P	-1.191031755	2.023983283	1.228485138
C	2.175654329	2.336394737	3.782611956
C	3.861220006	1.740549692	1.55194407
C	3.165621961	4.463768952	2.150869186
C	-1.518414273	1.52609304	2.991045702
C	-1.847326521	0.54749401	0.325315388
C	-2.541827765	3.261664376	0.963376317
H	1.784202478	3.185862758	-0.50298286
H	0.141991678	2.837310708	-0.854595287
H	2.418789038	5.175788047	2.515042873
H	3.494714396	4.798147494	1.163848634
H	4.017865841	4.456764362	2.840035979
H	4.202679657	2.01191418	0.549864121
H	3.56636273	0.686973159	1.532730501
H	4.681828249	1.868364897	2.267184493
H	1.836601833	1.299089853	3.864233549
H	1.410831617	2.977343469	4.23213305
H	3.106679341	2.448297117	4.350541202
H	-1.292521559	2.362295951	3.659906679
H	-0.868061477	0.689750463	3.265567023
H	-2.561609395	1.225301164	3.14313952
H	-2.56424912	3.541107697	-0.092961086
H	-2.332379365	4.164210627	1.545513299
H	-3.519700487	2.865007723	1.259490303
H	-1.184326432	-0.307405299	0.489355094
H	-1.857135936	0.763676514	-0.745914571
H	-2.858261309	0.283986663	0.656810888

Table 9. Cartesian Coordinates for Geometry Optimized $Ni(PMe_3)_3H_2$

$Ni(PMe_3)_3H_2$

E^{SCF} = -1554.10951905679 Hartrees

G = -1553.569498 Hartrees

atom	x	y	z
Ni	7.793186818	5.516270202	20.88444238
P	8.415355374	6.307909455	18.9023089
H	6.958688682	6.768828401	21.06412032
P	8.976193891	5.965189269	22.7101771
H	8.635757559	4.263131594	20.7278071
P	5.954895418	4.259203372	21.00094186
C	9.184246684	7.997918367	18.87778829
H	10.10673096	7.988965745	19.46622618
H	8.493779456	8.708059137	19.3415531
H	9.417726959	8.330333574	17.85905653
C	7.070077815	6.551427835	17.64487879
H	7.452726745	6.979177449	16.71035338
H	6.309800936	7.218355382	18.06156566
H	6.595458971	5.590283336	17.42471186
C	10.80530776	6.191576282	22.48236067
H	11.31898341	6.368959706	23.43499619
H	10.99012726	7.041142711	21.81812221
H	11.21801428	5.295243963	22.01068553
C	8.565055598	7.482306579	23.69638531
H	7.522957208	7.423642288	24.02390979
H	8.659557159	8.36247694	23.05383938
H	9.214418003	7.600537219	24.57238174

C	9.651464711	5.355890497	17.89767004
H	9.261962174	4.350913792	17.7109051
H	10.57436693	5.24950617	18.47530287
H	9.876866379	5.842182052	16.94072712
C	8.981271585	4.680506524	24.05118891
H	9.331838151	3.73209735	23.63408767
H	7.963307325	4.532295423	24.4226216
H	9.626628905	4.967740991	24.89005316
C	5.90462864	2.722428357	19.96102985
H	6.750036546	2.084273038	20.23304218
H	6.016780519	2.992521414	18.90664375
H	4.969130674	2.164393405	20.08894566
C	4.337269863	5.042402453	20.53845209
H	3.496983163	4.342831135	20.6246562
H	4.39301311	5.409800995	19.50950621
H	4.16215376	5.903668986	21.189373
C	5.506346169	3.54117076	22.65553766
H	5.353965918	4.351467918	23.37487702
H	6.328248233	2.91504089	23.01439979
H	4.592924208	2.936237745	22.60359794

Table 10. Cartesian Coordinates for Geometry Optimized $(HCO_2H)_2$

$(HCO_2H)_2$

E^{SCF} = -379.70363522849 Hartrees

G = -379.531621 Hartrees

atom	**x**	**y**	**z**
O	1.6304795795	0.1796667777	0.1525427533
O	0.5084787833	-0.3594388271	-1.7415186988

H	-0.3119565098	-0.3000157837	-1.1632647553
C	1.5904112561	-0.0994091320	-1.0421929999
H	2.5000031877	-0.1571748586	-1.6532147290
O	-1.6304795795	-0.1796667777	-0.1525427533
O	-0.5084787833	0.3594388271	1.7415186988
H	0.3119565098	0.3000157837	1.1632647553
C	-1.5904112561	0.0994091320	1.0421929999
H	-2.5000031877	0.1571748586	1.6532147290

Table 11. Cartesian Coordinates for Geometry Optimized H_2

H_2

E^{SCF} = -1.18001891959 Hartrees

G = -1.180338 Hartrees

atom	**x**	**y**	**z**
H	0.0000000000	0.0000000000	0.371880458
H	0.0000000000	0.0000000000	-0.371880458

Table 12. Cartesian Coordinates for Geometry Optimized CO_2

CO_2

E^{SCF} = -188.65715586048 Hartrees

G = -188.596583 Hartrees

atom	**x**	**y**	**z**
O	0.0000000000	0.0000000000	1.1696716049
C	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	-1.1696716049

Table 13. Cartesian Coordinates for Geometry Optimized PMe_3

PMe_3

E^{SCF} = -461.17944670422 Hartrees

G = -461.030132 Hartrees

atom	x	y	z
P	10.69844153	2.95104194	7.285514591
C	9.789851568	4.435030854	7.959224304
C	9.897121613	1.610822162	8.307041707
C	12.30627149	3.126797481	8.215743434
H	12.15635563	3.253935325	9.295124314
H	12.85812506	3.991516229	7.832789122
H	12.92516853	2.239131544	8.048560304
H	8.859526173	1.475661037	7.98444313
H	9.905878628	1.837708759	9.380424692
H	10.42037897	0.663007928	8.143421852
H	9.805734968	4.476159226	9.05546258
H	8.748058543	4.410259086	7.623078846
H	10.24240094	5.351296283	7.566033906