**Supplementary Material**

Dibromomanganese(II) complexes with hexamethylphosphoramide and phenylphosphonic bis(diamide) ligands

M. BORTOLUZZI and J. CASTRO\*

**xyz coordinates calculated by DFT methods**

xyz coordinates of compound [MnBr2{O=P(NMe2)3}2], gas phase (61 atoms)

Mn 0.000058896 2.049595068 -0.000659918

Br -1.085510161 3.108390865 1.958413880

Br 1.085900845 3.106947553 -1.960334972

N -2.453025220 -0.448190734 1.562436580

N 2.453314738 -0.448542484 -1.562471347

N 2.541654482 -1.638363123 0.798526713

N -2.542012271 -1.638490103 -0.798358056

N -4.033267412 0.581142736 -0.370281668

N 4.033278415 0.581020438 0.370320476

P 2.569778550 -0.139127282 0.066158647

P -2.569789146 -0.139121965 -0.066244718

O -1.444242693 0.700646771 -0.640942970

O 1.444264386 0.700995487 0.640411928

C -1.149378453 -0.815799418 2.097663834

C 1.149699516 -0.816133370 -2.097852878

C 2.308816483 -1.708564633 2.229479475

C -2.309620323 -1.708877834 -2.229373646

C 2.968671670 -2.873700089 0.178499400

C -2.968884309 -2.873724954 -0.178037996

C -3.360567792 0.127240111 2.543942615

C 3.361157198 0.126451572 -2.543948283

C -4.182987717 2.024842276 -0.259691392

C 4.183127725 2.024686339 0.259422830

C 5.257908294 -0.157188090 0.584981319

C -5.258035350 -0.157007503 -0.584394869

H -0.492585374 -1.192080905 1.299113967

H 0.492672934 -1.192059977 -1.299298108

H -0.650782499 0.058112340 2.554028914

H 0.651331116 0.057681248 -2.554644151

H -1.264392573 -1.607781433 2.858880808

H 1.264756053 -1.608384072 -2.858785690

H 1.553642644 -2.481891401 2.456317655

H -1.554720060 -2.482416005 -2.456391566

H 1.930182694 -0.744476204 2.594881433

H -1.930881852 -0.744904277 -2.594973803

H 2.201767547 -3.656908440 0.314969709

H -2.201990028 -3.656940110 -0.314515515

H -2.967120284 1.078723234 2.942432164

H 2.967962103 1.077902780 -2.942767619

H 3.122084504 -2.723949373 -0.898344233

H -3.122119572 -2.723800613 0.898805456

H -3.227594159 2.497505427 0.007145902

H 3.227879990 2.497346668 -0.007936215

H 3.232737233 -1.962571822 2.782768491

H -3.233775643 -1.962704894 -2.782364454

H -3.495509131 -0.585374290 3.375208684

H 3.496138927 -0.586400436 -3.375007550

H 3.912265710 -3.251285966 0.617603552

H -3.912542621 -3.251396427 -0.616930748

H -4.346163128 0.313294359 2.096782106

H 4.346684341 0.312434172 -2.096611898

H 4.533432958 2.449195559 1.215800026

H -4.533697174 2.449114720 -1.216019733

H -4.914591223 2.284378610 0.526847478

H 4.915104136 2.283972589 -0.526853846

H 5.047529526 -1.217666699 0.781663918

H -5.047822596 -1.217568815 -0.780816816

H 5.794474948 0.247311970 1.460448781

H -5.794781824 0.247285230 -1.459846421

H -5.939964989 -0.095051085 0.285826604

H 5.940057015 -0.095573296 -0.285092266

xyz coordinates of compound [MnBr2{O=P(NMe2)3}2], solution in CH2Cl2 (61 atoms)

Mn 0.001066888 2.023082813 0.000686454

Br -0.992748023 3.293900034 1.923674840

Br 0.995202918 3.293119745 -1.922534145

N 2.415595173 -0.404606660 -1.530562050

N -2.417225007 -0.400984390 1.531634049

N 2.444318095 -1.605423850 0.824281997

N -2.445021478 -1.605226706 -0.822109907

N -4.049426776 0.544578419 -0.402911827

N 4.051904632 0.541567775 0.400116287

P -2.563951589 -0.118832775 -0.095910862

P 2.564865485 -0.119947542 0.096549292

O -1.487675596 0.803606234 -0.669478434

O 1.491122639 0.804872976 0.670967163

C 1.120898530 -0.810418631 -2.057025473

C -1.123881536 -0.807825515 2.060523524

C 2.255090401 -1.664224678 2.265363324

C -2.256004646 -1.665916687 -2.263140391

C 2.817960239 -2.863499369 0.202888290

C -2.818182221 -2.862495583 -0.198893920

C 3.323493513 0.154330697 -2.520167808

C -3.326980731 0.158349459 2.519215102

C -4.262959646 1.979297563 -0.288044121

C 4.267431487 1.975910567 0.284367512

C -5.251214580 -0.256137009 -0.543952786

C 5.252726573 -0.261179942 0.538050179

H 0.484497879 -1.218086841 -1.257339405

H -0.486068977 -1.215189254 1.261822440

H 0.587542499 0.045874088 -2.508703294

H -0.591169665 0.048027061 2.513796007

H 1.253216597 -1.591413128 -2.825251017

H -1.258226608 -1.589348432 2.827801183

H 1.493649064 -2.422631177 2.514347571

H -1.494192337 -2.424245969 -2.511294093

H 1.907417568 -0.692386280 2.640188496

H -1.908998745 -0.694460750 -2.639635876

H 2.018431261 -3.609568455 0.350196295

H -2.018666555 -3.608686139 -0.345674959

H 2.935438322 1.103308552 -2.931213686

H -2.939850171 1.107831925 2.929982625

H -2.973215689 -2.725182886 0.879028094

H 2.973491632 -2.727567513 -0.875131930

H 3.191711302 -1.934156877 2.786743972

H -3.192643465 -1.936998187 -2.783874995

H -3.310444564 2.496084961 -0.107759036

H 3.314858345 2.494295604 0.109162955

H 3.449448009 -0.564938848 -3.346071010

H -3.453875952 -0.560272007 3.345536087

H 3.747551110 -3.270476926 0.641401925

H -3.747898419 -3.270436607 -0.636386047

H 4.312276387 0.340045861 -2.080940180

H -4.315216930 0.343160393 2.078321527

H -4.706956328 2.375490493 -1.216993495

H 4.717073747 2.370746733 1.211135249

H -4.944559604 2.213860878 0.549569721

H 4.944932306 2.209829287 -0.556829594

H -4.997803891 -1.308148447 -0.733824414

H 4.998148490 -1.311777150 0.734353123

H -5.844713801 0.107344681 -1.399323334

H 5.851276909 0.105191573 1.388606186

H 5.885818602 -0.219672394 -0.367936338

H -5.888703071 -0.209144767 0.358592956

xyz coordinates of compound [MnBr2{O=PPh(NMe2)2}2], Mol. **a**, gas phase(65 atoms)

Mn 0.059151419 -1.730183871 -0.790739587

Br 0.529164115 -3.046365264 1.259084082

Br 0.751823367 -2.056845645 -3.130445412

N -2.191158112 1.441187916 -0.109216942

N 2.235221351 1.511142917 1.620895344

N -2.424043886 -0.338387739 1.821941445

N 2.585190031 2.024740478 -0.951877331

P 2.269989295 0.777382602 0.122596171

P -2.647524402 -0.133884923 0.186340294

O 0.994663066 0.082042576 -0.310328166

O -1.902115168 -1.059484935 -0.762553672

C -1.187582314 0.124299929 2.444757296

C -1.547956475 1.807168697 -1.359924178

C 1.626440764 2.813799059 1.821580526

C 2.246985404 1.800011285 -2.354607638

C 2.288415795 0.678390056 2.816857845

C -2.712774241 2.545541587 0.667208017

C -2.971679419 -1.532724665 2.462042922

C 3.689831816 -0.342485095 0.166387666

C 3.690391241 -1.476785715 -0.653697405

C 3.768116875 2.846571310 -0.763091020

C -4.420481714 -0.351298355 -0.096827056

C 4.814622194 -2.299517128 -0.699583682

C -4.825203206 -1.059188298 -1.233183916

C 4.829690423 -0.034116214 0.923224901

C -5.382466756 0.226146710 0.742375164

C 5.938587698 -1.996314519 0.064144218

C 5.947743581 -0.860653558 0.874575375

C -6.181609384 -1.180856981 -1.531185625

C -6.735683125 0.100750162 0.441718224

C -7.134644546 -0.600700327 -0.696879282

H -0.489972835 -0.718715873 2.590556360

H 0.615945271 2.723341442 2.262774947

H -0.619657704 2.370605930 -1.159150415

H -0.688856581 0.859824602 1.798312175

H -1.277297600 0.906633181 -1.925900679

H 1.327024161 0.718352348 3.356820217

H -1.410502683 0.589555596 3.421373939

H 1.447264131 1.052869665 -2.445779556

H 1.537954312 3.347795247 0.866031180

H 1.909827884 2.745350024 -2.811004880

H -1.917172026 3.292534223 0.837080660

H -2.216163175 2.430786557 -1.981346794

H 2.241903947 3.421291371 2.507436129

H -2.246627876 -2.364667444 2.422803493

H 2.474941364 -0.374928126 2.561017126

H 2.825954358 -1.722066485 -1.279470994

H -3.061302939 2.196938435 1.649666997

H 3.083036474 1.021181839 3.502411049

H 3.119577775 1.429807933 -2.924526486

H -3.205371958 -1.307419648 3.515402503

H -3.553368091 3.053712614 0.157293896

H 3.625543033 3.814655251 -1.269774738

H -3.901165839 -1.848271841 1.969351409

H 3.941335901 3.044544547 0.304240592

H -4.064767134 -1.514889956 -1.873596579

H 4.677700255 2.371709375 -1.179050344

H 4.801151174 -3.186475562 -1.337982424

H 4.836922562 0.852683318 1.564388626

H -5.072300676 0.760787985 1.645522015

H -6.494023524 -1.736808107 -2.419081778

H 6.816106434 -2.648338791 0.029356854

H 6.830171793 -0.619757742 1.473582572

H -7.484267975 0.547241372 1.101859249

H -8.198367898 -0.699555332 -0.931054898

xyz coordinates of compound [MnBr2{O=PPh(NMe2)2}2], mol. **a**, solution in CH2Cl2 (65 atoms)

Mn -0.003774511 -1.801025268 -0.916857774

Br 0.203041137 -3.656849674 0.744220136

Br 0.746966513 -2.219291473 -3.257452522

N -2.018303756 1.399722844 0.031069972

N 2.132651343 1.537779078 1.550608823

N -2.363289217 -0.566402305 1.754646180

N 2.427157941 1.853404962 -1.047413123

P 2.246016061 0.687587895 0.130770896

P -2.591308904 -0.156696679 0.163366503

O 1.062722430 -0.201047491 -0.231168628

O -1.905400258 -1.032518928 -0.890627715

C -1.102439997 -0.256467269 2.421971486

C 1.351425484 2.762812685 1.650827311

C -1.433836314 1.864634562 -1.217840471

C 2.094289940 1.520473878 -2.427333711

C 2.382114696 0.893320273 2.833741986

C -2.535454220 2.451248701 0.890886155

C -3.028680572 -1.744744552 2.303159257

C 3.478568446 2.852739075 -0.924475739

C 3.747706971 -0.312916919 0.266931255

C 3.757903117 -1.614926620 -0.246272446

C -4.372254708 -0.220420948 -0.127139419

C -4.837430003 -0.756293009 -1.333320432

C 4.928348035 0.232269643 0.793806207

C 4.933090825 -2.365432186 -0.227902793

C -5.281545348 0.330299724 0.787079019

C 6.099482963 -0.520280489 0.810004793

C 6.102036797 -1.819971082 0.299650322

C -6.201095279 -0.737798036 -1.624730908

C -6.642420611 0.344688534 0.492555259

C -7.101659616 -0.186784235 -0.714278984

H 0.377570762 2.577108003 2.139425586

H -0.437100732 -1.138625173 2.433827032

H -0.517237696 2.443280693 -1.011902261

H -0.582921300 0.553623328 1.893760593

H -1.161569547 1.011431411 -1.850792737

H 1.167880819 3.189951633 0.656305573

H -1.300869542 0.055778995 3.460674588

H 1.353747759 0.711626554 -2.464399821

H 1.437261006 0.719810896 3.377655945

H 1.673886479 2.407637596 -2.928276499

H -1.752390193 3.210425671 1.051151394

H 1.899606829 3.505474597 2.253726716

H -2.138242604 2.507996728 -1.775357942

H -2.387883486 -2.638813909 2.205515641

H -2.820599070 2.045923879 1.871920176

H 2.847847835 -2.050700612 -0.666671416

H 2.881112363 -0.075717221 2.701889203

H 2.987898882 1.194517082 -2.991393604

H 3.027337314 1.532354674 3.459028467

H 3.183730355 3.758872097 -1.476571498

H -3.246520898 -1.576885159 3.369939617

H -3.414668454 2.954685389 0.446882978

H 3.635991385 3.130229713 0.126763747

H -3.979317928 -1.938021693 1.788473846

H -4.124267226 -1.189254696 -2.039868765

H 4.438979950 2.492993277 -1.339684030

H -4.928315570 0.735248576 1.740272464

H 4.930182055 -3.383221466 -0.626736151

H 4.931047941 1.245437564 1.207210344

H -6.561209351 -1.157624775 -2.567772666

H 7.015257154 -0.092102428 1.226202501

H 7.021970819 -2.411155799 0.315927623

H -7.349675890 0.769848349 1.209855224

H -8.170869609 -0.173558470 -0.944312762

xyz coordinates of compound [MnBr2{O=PPh(NMe2)2}2], mol. **b**, gas phase(65 atoms)

Mn 0.000768839 2.207518997 -0.704885289

Br 0.191977781 1.829152224 -3.161607106

Br 0.650717298 4.272920968 0.446227895

N -1.575213057 -0.930159220 1.175051148

N -1.995813970 -1.013854570 -1.431350899

N 3.361142922 1.550840339 1.392988993

N 3.551990527 1.054950783 -1.183207782

P -2.278033399 -0.082725039 -0.086762758

P 2.727359423 0.602627923 0.182689001

O 1.206744166 0.715107885 0.178843048

O -1.775721951 1.353402564 -0.065076720

C -0.678741316 -1.595771514 -1.679887992

C -1.137773845 -0.193683781 2.351055928

C -1.932298163 -2.312959607 1.424559055

C 2.151832785 -1.989604739 0.962141085

C 2.460524927 -3.305771776 1.302511645

C 2.547781284 1.939884210 2.532875255

C -2.719195314 -0.704966719 -2.663786846

C 3.151211988 -1.134777474 0.483502319

C 3.565361849 0.198509538 -2.364873550

C 3.695005123 2.477892334 -1.498387835

C 3.765795507 -3.774688194 1.166596806

C -4.074874081 -0.039527851 0.117737722

C 4.461507047 -1.611332783 0.351131461

C -4.670072622 1.169351837 0.493287032

C 4.765867870 -2.927182981 0.689073292

C 4.791590517 1.662367510 1.593735917

C -4.863081563 -1.190611131 -0.014803776

C -6.040703294 1.223407124 0.741408143

C -6.231353459 -1.131872714 0.233657288

C -6.819385328 0.075145647 0.614694789

H -0.079420354 -0.941826940 -2.336609668

H -0.133286134 -1.730061897 -0.738037407

H -0.212388783 -0.643836160 2.749029574

H -0.802959787 -2.579711080 -2.162496192

H -0.921476456 0.847597428 2.082705895

H -1.093005780 -2.824064254 1.927038039

H 1.131054234 -1.606077717 1.061110281

H 1.484453750 1.835967499 2.288126533

H 1.676243263 -3.971589463 1.674314049

H -1.903153656 -0.208351504 3.150122841

H -2.129032771 -2.838468214 0.478950179

H -2.139376874 -0.005981466 -3.291081498

H 2.721300117 3.002231751 2.767354754

H 2.772180738 0.497174102 -3.071690311

H 2.785882938 1.328685446 3.424350069

H -2.825503548 -2.407670008 2.072607667

H -2.894112130 -1.637096717 -3.225944967

H 2.989774741 2.768357573 -2.295694302

H 3.409899657 -0.854162999 -2.090529357

H 3.474277898 3.095908006 -0.617040605

H -3.695846323 -0.252647817 -2.443781919

H 4.007146583 -4.807683338 1.432333792

H -4.046696000 2.063378077 0.580232598

H -4.406754165 -2.133348455 -0.332171241

H 4.545136629 0.279917418 -2.865105308

H 4.724771076 2.682749050 -1.836924192

H 5.037491260 2.679716538 1.939811765

H 5.163777135 0.942898948 2.349008729

H 5.245802918 -0.951782789 -0.033423068

H 5.329232405 1.488679363 0.651130290

H 5.789109002 -3.295444527 0.577205263

H -6.502090420 2.170993891 1.031741846

H -6.844066777 -2.030891573 0.125555099

H -7.894712882 0.120302034 0.809553500

xyz coordinates of compound [MnBr2{O=PPh(NMe2)2}2], mol. **b**, solution in CH2Cl2 (65 atoms)

Mn -0.032980614 2.204188554 -0.650878241

Br 0.134280150 2.123800617 -3.156579930

Br 0.408993057 4.404131040 0.426360891

N -1.552195862 -0.918668497 1.165557109

N -1.965549180 -0.974752262 -1.443930149

N 3.433645381 1.614279339 1.352789655

N 3.573111816 1.045595488 -1.213080269

O 1.243797433 0.829152271 0.180216925

O -1.809302963 1.369476638 -0.059502389

P -2.284970262 -0.086594163 -0.081823808

P 2.763896130 0.647144169 0.176693829

C -0.633706788 -1.518265254 -1.695158497

C -1.175503954 -0.187588569 2.368241983

C -1.872279476 -2.319720634 1.392652900

C 2.087140694 -1.896950930 1.019195154

C 2.346602053 -3.218743333 1.379762038

C 2.644600401 1.992436306 2.515836925

C -2.710302568 -0.698928041 -2.669649578

C 3.114977263 -1.094314393 0.508909344

C 3.520140942 0.170965198 -2.380008382

C 3.630758004 -3.742335456 1.232616737

C 3.790133919 2.450902821 -1.550397948

C -4.079584549 -0.082825871 0.117936721

C 4.404381135 -1.624123449 0.365490414

C 4.658489736 -2.945738583 0.724378180

C -4.709614137 1.103187452 0.511788140

C -4.832990503 -1.256280882 -0.029680321

C 4.871093129 1.604396724 1.572844314

C -6.081769088 1.114727164 0.759938989

C -6.203075803 -1.239498260 0.218505426

C -6.826768551 -0.054789639 0.615370364

H -0.046130056 -0.840907114 -2.340248152

H -0.088493403 -1.656350233 -0.753814390

H -0.278333810 -0.650547274 2.810806673

H -0.728616163 -2.494649616 -2.196694841

H -0.936783991 0.853721772 2.120593605

H -1.021308387 -2.811007271 1.892979233

H 1.083233579 -1.473574316 1.126248730

H 1.542059670 -3.845053991 1.776030767

H 1.580405253 2.033985510 2.254230851

H -1.980884217 -0.202662501 3.126164926

H -2.050528486 -2.837636742 0.439755130

H -2.172098462 0.031546443 -3.299073661

H 2.720920745 0.488602719 -3.072541370

H -2.764127410 -2.444113714 2.035463278

H 2.787842770 1.286766379 3.355965482

H -2.836754294 -1.634517314 -3.237481201

H 2.950039135 2.996806022 2.848982471

H 3.035062598 2.800873097 -2.276296470

H 3.332353781 -0.870413098 -2.085234300

H -3.707952586 -0.298650015 -2.444811240

H 3.721087890 3.076693981 -0.650688646

H 3.833955655 -4.779428693 1.514122969

H -4.117797664 2.016120852 0.618018039

H -4.352267392 -2.184326602 -0.354014978

H 4.485564792 0.207483894 -2.910094070

H 4.791553536 2.574638740 -1.993369060

H 5.174170403 0.830682618 2.303723585

H 5.187284266 2.585857741 1.960072248

H 5.211748427 -1.007437225 -0.041339057

H 5.405384668 1.423654089 0.629711471

H 5.663977594 -3.357615681 0.604444720

H -6.570361488 2.043908757 1.065227267

H -6.788145462 -2.155191884 0.098727965

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