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Supporting Information

p-Bonding in Complexes of Benzannulated Biscarbenes, -Bermylenes and -Stannylenes: An Experimental and Theoretical Study

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Supplemental Material for Π-Bonding in Complexes of Benzannulated Biscarbenes, -germylenes and -stannylenes: an Experimental and Theoretical Study

XYZ-coordinates and BP86/TZ2P energies of calculated structures

3M-C

46

-11,537499

Mo	0,000000	0,000000	1,656971
C	-2,051170	0,000000	1,660787
O	-3,211490	0,000000	1,680788
C	0,000000	1,300226	3,177271
O	0,000000	1,978384	4,130776
C	0,000000	-1,300226	3,177271
O	0,000000	-1,978384	4,130776
C	2,051170	0,000000	1,660787
O	3,211490	0,000000	1,680788
C	0,000000	-1,494298	-0,000884
C	0,000000	1,494298	-0,000884
N	0,000000	-1,247025	-1,359474
C	0,000000	-2,423087	-2,112715
C	0,000000	-5,043635	-2,977755
C	0,000000	-2,658383	-3,487290
C	0,000000	-3,470824	-1,181849
C	0,000000	-4,801956	-1,601885
C	0,000000	-3,991874	-3,906170
H	0,000000	-1,847305	-4,213250
H	0,000000	-5,627588	-0,893091
H	0,000000	-4,216078	-4,971271
H	0,000000	-6,071829	-3,335375
C	0,000000	2,423087	-2,112715
C	0,000000	5,043635	-2,977755
C	0,000000	2,658383	-3,487290
C	0,000000	3,470824	-1,181849
C	0,000000	4,801956	-1,601885
C	0,000000	3,991874	-3,906170
H	0,000000	1,847305	-4,213250
H	0,000000	5,627588	-0,893091
H	0,000000	4,216078	-4,971271
H	0,000000	6,071829	-3,335375
N	0,000000	1,247025	-1,359474
N	0,000000	2,871814	0,074377
N	0,000000	-2,871814	0,074377
C	0,000000	0,000000	-2,095426
H	-0,888709	0,000000	-2,748456
H	0,888709	0,000000	-2,748456
C	0,000000	-3,642898	1,312179
H	0,890072	-3,415323	1,905473

H	-0,890072	-3,415323	1,905473
H	0,000000	-4,705910	1,056887
C	0,000000	3,642898	1,312179
H	-0,890072	3,415323	1,905473
H	0,890072	3,415323	1,905473
H	0,000000	4,705910	1,056887

3M-Ge

46

-11,2384808

Mo	0,000000	0,000000	2,180528
C	-2,051929	0,000000	2,263868
O	-3,203868	0,000000	2,365789
C	0,000000	1,449570	3,560023
O	0,000000	2,301116	4,349981
C	0,000000	-1,449570	3,560023
O	0,000000	-2,301116	4,349981
C	2,051929	0,000000	2,263868
O	3,203868	0,000000	2,365789
Ge	0,000000	-1,561999	0,190115
Ge	0,000000	1,561999	0,190115
N	0,000000	-1,235521	-1,654338
C	0,000000	-2,414731	-2,399564
C	0,000000	-4,922831	-3,647179
C	0,000000	-2,505493	-3,799603
C	0,000000	-3,603334	-1,614039
C	0,000000	-4,851278	-2,254283
C	0,000000	-3,756648	-4,417320
H	0,000000	-1,607357	-4,412833
H	0,000000	-5,770293	-1,672198
H	0,000000	-3,818066	-5,504261
H	0,000000	-5,897569	-4,132410
C	0,000000	2,414731	-2,399564
C	0,000000	4,922831	-3,647179
C	0,000000	2,505493	-3,799603
C	0,000000	3,603334	-1,614039
C	0,000000	4,851278	-2,254283
C	0,000000	3,756648	-4,417320
H	0,000000	1,607357	-4,412833
H	0,000000	5,770293	-1,672198
H	0,000000	3,818066	-5,504261
H	0,000000	5,897569	-4,132410
N	0,000000	1,235521	-1,654338
N	0,000000	3,364356	-0,246897
N	0,000000	-3,364356	-0,246897
C	0,000000	0,000000	-2,421398

H	-0,887833	0,000000	-3,078787
H	0,887833	0,000000	-3,078787
C	0,000000	-4,434325	0,751167
H	0,890687	-4,374698	1,388922
H	-0,890687	-4,374698	1,388922
H	0,000000	-5,414201	0,266744
C	0,000000	4,434325	0,751167
H	-0,890687	4,374698	1,388922
H	0,890687	4,374698	1,388922
H	0,000000	5,414201	0,266744

3M-Sn

46

-11,1460638

Mo	0,000000	0,000000	2,405348
C	-2,047695	0,000000	2,508851
O	-3,196520	0,000000	2,644500
C	0,000000	1,420451	3,796723
O	0,000000	2,242513	4,617475
C	0,000000	-1,420451	3,796723
O	0,000000	-2,242513	4,617475
C	2,047695	0,000000	2,508851
O	3,196520	0,000000	2,644500
Sn	0,000000	-1,666869	0,239434
Sn	0,000000	1,666869	0,239434
N	0,000000	-1,245622	-1,794674
C	0,000000	-2,406003	-2,570758
C	0,000000	-4,833097	-4,005805
C	0,000000	-2,416593	-3,978616
C	0,000000	-3,658573	-1,870762
C	0,000000	-4,853104	-2,613917
C	0,000000	-3,614851	-4,688949
H	0,000000	-1,481241	-4,531415
H	0,000000	-5,812430	-2,101877
H	0,000000	-3,593016	-5,777406
H	0,000000	-5,772983	-4,555512
C	0,000000	2,406003	-2,570758
C	0,000000	4,833097	-4,005805
C	0,000000	2,416593	-3,978616
C	0,000000	3,658573	-1,870762
C	0,000000	4,853104	-2,613917
C	0,000000	3,614851	-4,688949
H	0,000000	1,481241	-4,531415
H	0,000000	5,812430	-2,101877
H	0,000000	3,593016	-5,777406
H	0,000000	5,772983	-4,555512

N	0,000000	1,245622	-1,794674
N	0,000000	3,582605	-0,486287
N	0,000000	-3,582605	-0,486287
C	0,000000	0,000000	-2,550752
H	-0,887498	0,000000	-3,208803
H	0,887498	0,000000	-3,208803
C	0,000000	-4,766022	0,375580
H	0,890205	-4,783599	1,018045
H	-0,890205	-4,783599	1,018045
H	0,000000	-5,688608	-0,210684
C	0,000000	4,766022	0,375580
H	-0,890205	4,783599	1,018045
H	0,890205	4,783599	1,018045
H	0,000000	5,688608	-0,210684

Ligand in 3M-C

37

-8,7751821

C	-1,055996	2,092966	0,619579
C	0,109195	-1,552157	0,441704
N	-0,869879	1,267690	-0,466638
C	-0,011302	1,816004	-1,427994
C	1,709661	3,471996	-2,837598
C	0,458453	1,379586	-2,667183
C	0,374940	3,064081	-0,903864
C	1,241749	3,909980	-1,596264
C	1,322311	2,229135	-3,363282
H	0,180416	0,411038	-3,078720
H	1,543585	4,873657	-1,188532
H	1,707325	1,914972	-4,332251
H	2,388847	4,105189	-3,406595
C	-0,538065	-2,005441	-1,734892
C	0,206845	-4,033631	-3,477014
C	-1,128096	-2,043308	-2,999472
C	0,404616	-2,976422	-1,347523
C	0,793927	-4,001302	-2,209822
C	-0,740014	-3,071672	-3,863144
H	-1,870543	-1,310405	-3,311466
H	1,524549	-4,750628	-1,908733
H	-1,185548	-3,128543	-4,855071
H	0,485508	-4,820947	-4,175615
N	-0,671785	-1,163078	-0,623175
N	0,760566	-2,653103	-0,036725
N	-0,281207	3,178858	0,323500
C	-1,557151	-0,007623	-0,551596
H	-2,206100	-0,030013	-1,435161

H	-2,165233	-0,065564	0,354681
C	-0,156738	4,322931	1,210136
H	-0,499018	5,240191	0,711974
H	-0,780384	4,126990	2,085868
H	0,886705	4,456323	1,526244
C	1,715198	-3,408292	0,758076
H	1,780615	-2,922760	1,734896
H	1,380365	-4,446787	0,884112
H	2,703953	-3,406010	0,279846

Ligand in 3M-Ge

37

-8,5260808

Ge	2,235838	-1,971875	0,169558
Ge	-0,882865	0,363245	1,429726
N	1,169406	-0,654915	-0,697351
C	1,765795	0,594459	-0,816019
C	3,258749	2,962873	-0,920168
C	1,215122	1,744703	-1,402630
C	3,076998	0,639520	-0,264555
C	3,816357	1,832800	-0,323376
C	1,965585	2,918847	-1,456810
H	0,202930	1,726121	-1,804241
H	4,820664	1,875717	0,094952
H	1,535447	3,808968	-1,913823
H	3,833752	3,886974	-0,963517
C	-2,515624	-0,381687	-0,716331
C	-5,272580	-0,278571	-1,228660
C	-3,024351	-0,865089	-1,933346
C	-3,408386	0,152883	0,257851
C	-4,785292	0,201979	-0,011934
C	-4,397296	-0,810160	-2,182812
H	-2,356938	-1,285797	-2,683834
H	-5,472370	0,611963	0,726913
H	-4,786274	-1,186462	-3,128077
H	-6,341924	-0,239991	-1,432854
N	-1,192797	-0,361981	-0,313108
N	-2,772481	0,575479	1,408933
N	3,489475	-0,561323	0,286511
C	-0,164942	-0,890549	-1,202982
H	-0,299209	-1,977004	-1,326491
H	-0,269582	-0,435330	-2,202375
C	4,810173	-0,663673	0,889422
H	4,922341	0,038556	1,729455
H	4,958275	-1,680179	1,270955
H	5,603736	-0,452177	0,156569

C	-3,550559	1,149666	2,495604
H	-4,292327	0,433473	2,881956
H	-2,879218	1,422874	3,317876
H	-4,085959	2,056620	2,174305

Ligand in 3M-Sn

37

-8,4522137

Sn	1,252789	1,141934	0,193107
Sn	-1,231521	-1,131243	0,151483
N	0,182547	1,177912	-1,643937
C	-0,280493	2,411961	-2,042742
C	-1,231890	5,011568	-2,594752
C	-0,903830	2,707072	-3,272876
C	-0,097341	3,472705	-1,087587
C	-0,593746	4,758022	-1,383550
C	-1,380130	3,988274	-3,539795
H	-1,008968	1,932039	-4,029281
H	-0,468494	5,561575	-0,659907
H	-1,861192	4,192668	-4,495384
H	-1,603201	6,012744	-2,809525
C	0,333981	-2,407281	-2,057995
C	1,244924	-5,019004	-2,618535
C	0,982382	-2,700089	-3,275658
C	0,104996	-3,475039	-1,120771
C	0,582056	-4,766861	-1,420372
C	1,438338	-3,987788	-3,546758
H	1,122833	-1,917894	-4,018835
H	0,421721	-5,576436	-0,710482
H	1,939310	-4,190806	-4,492331
H	1,600612	-6,025138	-2,836512
N	-0,113928	-1,168899	-1,656684
N	-0,585721	-3,135699	0,019631
N	0,571634	3,134199	0,066202
C	0,056029	0,006514	-2,498544
H	0,953655	-0,109178	-3,128267
H	-0,807687	0,124012	-3,173374
C	0,810327	4,156031	1,074355
H	-0,132710	4,557754	1,478637
H	1,376625	3,722904	1,907776
H	1,391924	4,999997	0,669937
C	-0,871143	-4,163405	1,009470
H	0,052827	-4,589412	1,432485
H	-1,449081	-3,727580	1,833459
H	-1,459918	-4,990351	0,580981

Mo(CO)4

9

-2,6392210

Mo	-1,749879	-0,137731	2,890535
C	-3,256279	-0,027337	1,704110
O	-4,176334	0,039217	0,990054
C	-1,841374	1,889758	3,141571
O	-1,963320	3,030076	3,294029
C	-2,996337	-0,341802	4,338032
O	-3,759550	-0,465032	5,211535
C	-1,749700	-2,168151	2,646450
O	-1,820362	-3,315048	2,511989

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benzannulated NHGe-NMe3 complex

34

-7,1772501

Ge	1,348822	-0,012811	0,194966
N	0,580092	-1,181265	1,491051
N	1,002624	1,319536	1,514356
C	0,364142	0,854217	2,652999
C	0,126508	-0,552760	2,639977
C	0,463190	-2,621846	1,363486
C	1,365508	2,720655	1,413063
C	-0,032613	1,613344	3,762599
C	-0,500650	-1,159283	3,737122
C	-0,889583	-0,385764	4,838409
C	-0,657261	0,990834	4,851035
H	0,149722	2,687274	3,782780
H	-0,958247	1,587931	5,711256
H	-1,372394	-0,866221	5,688779
H	-0,680874	-2,233759	3,737706
N	-0,962551	0,393642	-1,118946
C	-0,765600	1,595718	-1,929901
C	-1,173517	-0,788119	-1,955833
C	-2,046344	0,568298	-0,147197
H	-0,587980	-2,957817	1,378587
H	0,907545	-2,941611	0,413033
H	0,990828	-3,146222	2,177066
H	2,033421	3,028262	2,234371
H	1,893074	2,893897	0,467174
H	0,482765	3,382687	1,437297
H	-2,086849	-0,703883	-2,578840
H	-0,310719	-0,930106	-2,620307
H	-1,271786	-1,675755	-1,317749
H	-3,023899	0,740738	-0,641597
H	-2,121658	-0,326042	0,483248

H -1,822675 1,423229 0,502439
H -1,652323 1,832751 -2,551925
H -0,566116 2,452023 -1,272915
H 0,098206 1,456605 -2,593688
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benzannulated NHSn-NMe3 complex
34
-7,142512
Sn 1,568389 0,190305 0,099528
N 0,726519 -1,194637 1,434487
N 0,988146 1,434682 1,686143
C 0,318199 0,788262 2,712240
C 0,178801 -0,634351 2,577637
C 0,699391 -2,636832 1,272689
C 1,217800 2,864306 1,783947
C -0,210005 1,419891 3,851059
C -0,476079 -1,354411 3,591126
C -0,993749 -0,702022 4,715447
C -0,861816 0,681055 4,844575
H -0,105631 2,497965 3,964390
H -1,262040 1,192656 5,719049
H -1,497849 -1,281307 5,488085
H -0,579761 -2,434796 3,501337
N -0,868237 0,531692 -1,235206
C -0,603140 1,038191 -2,585143
C -1,503655 -0,790005 -1,279645
C -1,680832 1,479353 -0,461046
H 1,212876 -3,152399 2,101863
H -0,329136 -3,036602 1,223814
H 1,208925 -2,913663 0,341066
H 1,797601 3,126431 2,685104
H 1,786444 3,207921 0,910427
H 0,275641 3,439689 1,820124
H -2,492393 -0,755027 -1,778295
H -0,862601 -1,490518 -1,831541
H -1,633614 -1,164797 -0,257374
H -2,675886 1,635362 -0,922941
H -1,815443 1,102875 0,559918
H -1,165860 2,446537 -0,406264
H -1,536047 1,175057 -3,167022
H -0,088139 2,005679 -2,523453
H 0,045069 0,335846 -3,124993
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benzannulated NHGe
21
-4,698006

Ge	0,037890	-0,012540	0,300738
N	0,001266	-1,268988	1,719396
N	0,046010	1,257230	1,707956
C	0,023435	0,712990	2,978066
C	-0,001784	-0,712753	2,984494
C	-0,022809	-2,714887	1,562155
C	0,073307	2,701566	1,537399
C	0,023402	1,414392	4,194810
C	-0,026417	-1,402756	4,207479
C	-0,026122	-0,688810	5,406423
C	-0,001365	0,711669	5,400121
H	0,042609	2,503248	4,198931
H	-0,001367	1,259401	6,341749
H	-0,045332	-1,227727	6,352930
H	-0,045698	-2,491528	4,221332
H	0,855997	-3,185487	2,029462
H	-0,926224	-3,153870	2,013023
H	-0,017405	-2,965051	0,495181
H	-0,814129	3,176531	1,983519
H	0,968088	3,144993	2,000938
H	0,088018	2,941466	0,468161

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benzannulated NHSn

21

-4,660541

Sn	0,043648	-0,014164	0,052860
N	0,006715	-1,327345	1,681739
N	0,043908	1,314785	1,669313
C	0,021354	0,717489	2,912308
C	0,001118	-0,718017	2,919063
C	-0,012450	-2,780309	1,602504
C	0,065603	2,766898	1,576413
C	0,017073	1,408259	4,139581
C	-0,022386	-1,396883	4,152748
C	-0,026086	-0,688656	5,352513
C	-0,006412	0,711692	5,345937
H	0,032267	2,496821	4,144684
H	-0,009396	1,262950	6,285323
H	-0,044379	-1,230787	6,297026
H	-0,037733	-2,485351	4,168038
H	0,866672	-3,226561	2,094291
H	-0,914701	-3,201945	2,073717
H	-0,004566	-3,090555	0,550829
H	-0,824473	3,218172	2,043279
H	0,956889	3,192808	2,064352
H	0,082339	3,066866	0,521869

NMe3
13
-2,476735
N 0,000000 0,000000 0,050949
C -0,695223 1,204161 0,491987
C 1,390446 0,000000 0,491987
C -0,695223 -1,204161 0,491987
H 1,903805 -0,889633 0,102885
H 1,903805 0,889633 0,102885
H 1,493876 0,000000 1,601433
H -0,181458 -2,093560 0,102885
H -0,746938 -1,293734 1,601433
H -1,722347 -1,203927 0,102885
H -1,722347 1,203927 0,102885
H -0,746938 1,293734 1,601433
H -0,181458 2,093560 0,102885

XYZ-coordinates and RI-BP86/def-SVP energies of calculated structures
Model complex (CO)5Mo-CN2C2H2
20
-860,812946
Mo 0,000000 0,000000 -1,454890
C 0,000000 2,055515 -1,404857
C 2,046005 0,000000 -1,477453
C 0,000000 -2,055515 -1,404857
C 0,000000 0,000000 -3,488451
C 0,000000 0,000000 0,781419
C -2,046005 0,000000 -1,477453
O 0,000000 3,217306 -1,362867
O 0,000000 0,000000 -4,653058
O 0,000000 -3,217306 -1,362867
O 3,211788 0,000000 -1,499259
O -3,211788 0,000000 -1,499259
N -1,065580 0,000000 1,641721
N 1,065580 0,000000 1,641721
C -0,685870 0,000000 2,978079
C 0,685870 0,000000 2,978079
H -1,403379 0,000000 3,803302
H 1,403379 0,000000 3,803302
H -2,029069 0,000000 1,304790
H 2,029069 0,000000 1,304790

NHC fragment
9
-226,030134

C	0,000000	0,000000	1,467159
N	1,065580	0,000000	0,606857
N	-1,065580	0,000000	0,606857
C	0,685870	0,000000	-0,729501
C	-0,685870	0,000000	-0,729501
H	1,403378	0,000000	-1,554724
H	-1,403378	0,000000	-1,554724
H	2,029069	0,000000	0,943787
H	-2,029069	0,000000	0,943787

Model complex (CO)5Mo-SiN2C2H2

20

-1112,225683

Mo	0,000000	0,000000	1,697851
C	0,000000	2,057762	1,707311
C	-2,050612	0,000000	1,645105
C	0,000000	-2,057762	1,707311
C	0,000000	0,000000	3,726520
Si	0,000000	0,000000	-0,799372
C	2,050612	0,000000	1,645105
O	0,000000	3,218386	1,732738
O	0,000000	-3,218386	1,732738
O	-3,212102	0,000000	1,594457
O	3,212102	0,000000	1,594457
O	0,000000	0,000000	4,888623
N	1,216183	0,000000	-2,072679
N	-1,216183	0,000000	-2,072679
C	0,685220	0,000000	-3,361360
C	-0,685220	0,000000	-3,361360
H	1,334583	0,000000	-4,244891
H	-1,334583	0,000000	-4,244891
H	2,230484	0,000000	-1,951584
H	-2,230484	0,000000	-1,951584

NHSi fragment

9

-477,459936

Si	0,000000	0,000000	1,874055
N	1,216100	0,000000	0,600655
N	-1,216100	0,000000	0,600655
C	0,685180	0,000000	-0,688074
C	-0,685180	0,000000	-0,688074
H	1,334606	0,000000	-1,571675
H	-1,334606	0,000000	-1,571675
H	2,230354	0,000000	0,722067
H	-2,230354	0,000000	0,722067

Model complex (CO)5Mo-GeN2C2H2
20
-2899,809761

Mo	0,000000	0,000000	-1,844004
C	0,000000	2,058335	-1,856027
C	2,054049	0,000000	-1,824417
C	0,000000	-2,058335	-1,856027
C	0,000000	0,000000	-3,856526
Ge	0,000000	0,000000	0,732322
C	-2,054049	0,000000	-1,824417
O	0,000000	3,218414	-1,886118
O	0,000000	0,000000	-5,019764
O	0,000000	-3,218414	-1,886118
O	3,215957	0,000000	-1,815910
O	-3,215957	0,000000	-1,815910
N	-1,245851	0,000000	2,114732
N	1,245851	0,000000	2,114732
C	-0,687131	0,000000	3,382014
C	0,687131	0,000000	3,382014
H	-1,319807	0,000000	4,278762
H	1,319807	0,000000	4,278762
H	-2,262749	0,000000	2,016018
H	2,262749	0,000000	2,016018

NHGe fragment
9
-2265,059139

Ge	0,000000	0,000000	1,969396
N	1,245828	0,000000	0,586973
N	-1,245828	0,000000	0,586973
C	0,687148	0,000000	-0,680344
C	-0,687148	0,000000	-0,680344
H	1,320025	0,000000	-1,576936
H	-1,320025	0,000000	-1,576936
H	2,262769	0,000000	0,685611
H	-2,262769	0,000000	0,685611

Model complex (CO)5Mo-SnN2C2H2
20
-826,178363

Mo	0,000000	0,000000	-2,016766
C	0,000000	2,058809	-2,030168
C	2,054602	0,000000	-2,024333
C	0,000000	-2,058809	-2,030168
C	0,000000	0,000000	-4,014212

Sn	0,000000	0,000000	0,760745
C	-2,054602	0,000000	-2,024333
O	0,000000	3,218581	-2,069097
O	0,000000	0,000000	-5,178088
O	0,000000	-3,218581	-2,069097
O	3,215730	0,000000	-2,052794
O	-3,215730	0,000000	-2,052794
N	-1,307623	0,000000	2,386179
N	1,307623	0,000000	2,386179
C	-0,689762	0,000000	3,619240
C	0,689762	0,000000	3,619240
H	-1,290177	0,000000	4,540154
H	1,290177	0,000000	4,540154
H	-2,329736	0,000000	2,367825
H	2,329736	0,000000	2,367825

NHSn

9

-191,437979

Sn	0,000000	0,000000	-2,193454
N	-1,307658	0,000000	-0,567995
N	1,307658	0,000000	-0,567995
C	-0,689775	0,000000	0,665059
C	0,689775	0,000000	0,665059
H	-1,290184	0,000000	1,585984
H	1,290184	0,000000	1,585984
H	-2,329780	0,000000	-0,586323
H	2,329780	0,000000	-0,586323

Mo(CO)6

13

-747,995760

Mo	0,000000	0,000000	0,083798
C	0,000000	2,064751	0,089156
C	1,462511	0,000000	-1,374896
C	0,000000	-2,064751	0,089156
C	-1,462511	0,000000	-1,374896
C	1,457871	0,000000	1,545680
C	-1,457871	0,000000	1,545680
O	0,000000	3,222039	0,097453
O	-2,283041	0,000000	-2,191219
O	0,000000	-3,222039	0,097453
O	2,283041	0,000000	-2,191219
O	-2,272692	0,000000	2,367728
O	2,272692	0,000000	2,367728