

SUPPORTING INFORMATION

Part III

COMPUTATIONAL DATA

Molybdenum(VI) Nitrido Complexes with Tripodal Silanolate Ligands.

**Structure and Electronic Character of an Unsymmetrical Dimolybdenum
 μ -Nitrido Complex Formed by Incomplete Nitrogen Atom Transfer**

Daniel Rütter, Maurice van Gastel, Markus Leutzsch, Nils Nöthling, Daniel SantaLucia,^[+]

Frank Neese,* and Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, 45470 Mülheim/Ruhr, Germany

^[+] *Max-Planck-Institut für Chemische Energiekonversion, 45470 Mülheim/Ruhr, Germany*

Email: fuerstner@kofo.mpg.de; neese@kofo.mpg.de

DFT calculations

The electronic structure of **13a** and its electronic properties, was analyzed using DFT calculations using the B3LYP functional^{1,2} and the def2-TZVP basis set³ and effective core potentials⁴ at the molybdenum atoms.⁵ All calculations were carried out with ORCA version 5.0.4.⁶⁻⁹ The sets of unrestricted natural orbitals and localized quasi-restricted orbitals were constructed using the available functionality within ORCA with the UNO, qro and %loc keywords, respectively. The structures were fully optimized without constraints and confirmed to be minima on the potential energy surface through frequency calculations that showed only one negative modes at -9 cm^{-1} which was considered to be numerical noise. For calculation of the UVVIS spectrum, a TDDFT calculation was carried out using 400 roots. For calculation of the EPR g values,¹⁰ the all-electron basis set x2c-tzvpall^{11, 12} and the auxiliary basis set x2c/j^{11, 12} was used at the def2-TZVP optimized structure.

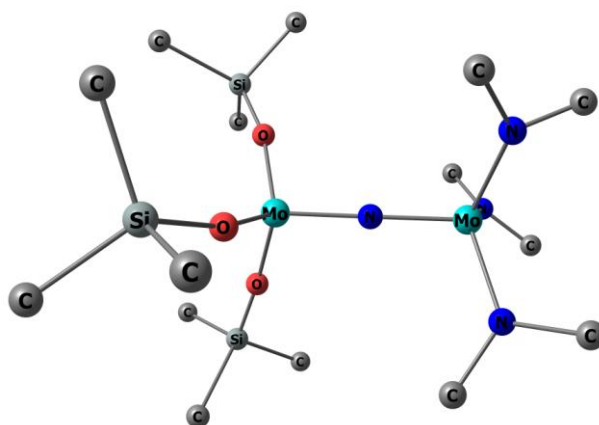


Figure S1. Computed geometric structure of **13a**; the ligand periphery was truncated for clarity.

Table S1. Selected bond distances [Å] and angles [°] of complex **13a**: comparison of the data from the X-ray crystal structure and the geometry optimized computed structure (B3LYP functional, Def2-TZVP basis set).

	SC-XRD	Optimized structure
$d(\text{Mo}^{\text{O}}-\mu\text{N})$	1.838	1.842
$d(\text{Mo}^{\text{N}}-\mu\text{N})$	1.808	1.780
$d(\text{Mo}^{\text{O}}-\text{O})$	1.910	1.907
	1.912	1.915
	1.920	1.927
$d(\text{Mo}^{\text{N}}-\text{N})$	1.970	1.978
	1.966	1.968
	1.968	1.970
$\angle(\text{Mo}^{\text{N}}-\mu\text{N}-\text{Mo}^{\text{O}})$	178.6	178.1
$\angle(\mu\text{N}-\text{Mo}^{\text{O}}-\text{O})$	102.7	101.9
	102.9	100.3
	102.3	103.0
$\angle(\mu\text{N}-\text{Mo}^{\text{N}}-\text{N})$	103.4	105.4
	104.6	105.0
	105.5	105.2

For completeness, an MO scheme using (non-localized) quasi-restricted orbitals is depicted in Figure S2. As expected, the two frontier molecular orbitals concern Mo-centered orbitals at -3.00 eV and -3.55 eV containing the 3 unpaired electrons. Below these, starting at -5.6 eV a plethora of ligand orbitals are found, involving either the ligating nitrogen and oxygen atoms, but also the phenyl moieties.

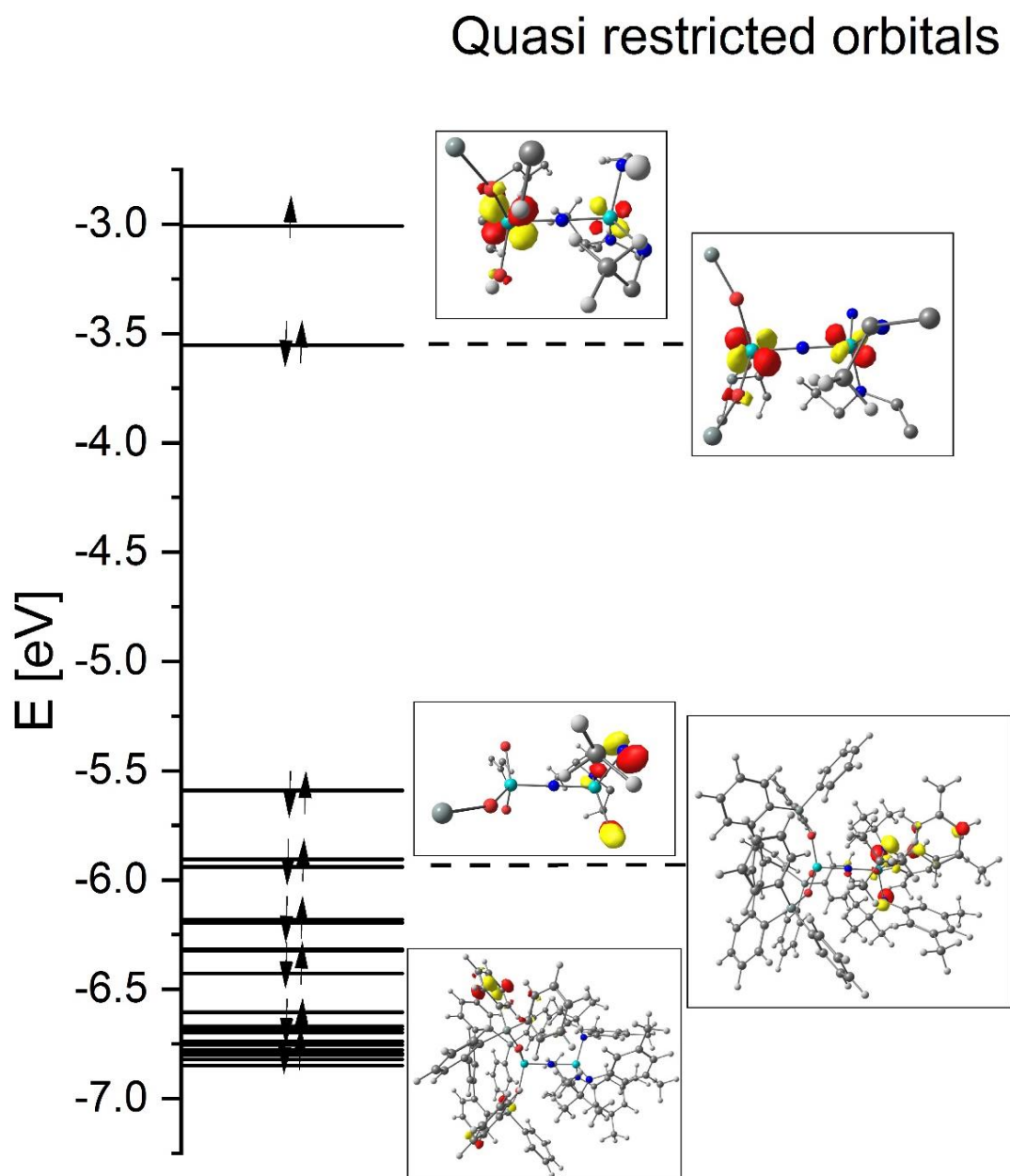


Figure S2. Molecular orbital scheme of **13a** including the frontier orbitals and the closest ligand orbitals. The structures have been truncated in the miniatures with the orbital contours for the purpose of clarity.

Def2-TZVP optimized coordinates [Å] of 13a

Mo	3.45586604664560	14.45721486589789	5.09046206209477
Mo	5.57901159156839	11.52404374112488	5.11317006873042
Si	8.86875144850438	12.70292045413374	4.72979871996492
Si	4.80347250106503	9.48649350468064	2.38319204850919
Si	5.19948629472491	9.93648872517479	8.17412160792142
O	5.43932022616038	10.99377536950186	6.94834458465146
O	7.30248002974735	12.26881628017402	4.68025286170564
O	4.88350115551632	10.51078544230666	3.65547284736519
N	3.61953091481247	15.17700232759893	3.26376972975143
N	4.47656906061412	12.99924946195447	5.11183382479362
N	4.13704728418030	15.59758805354526	6.55569163903166
N	1.63587111949035	13.80924573793881	5.46529475726391
C	3.62608522831284	16.60678206055411	3.27171671894458
C	3.89369313967196	14.50642750696165	1.95733411920439
C	9.07671087639900	14.45008909957510	4.06647876367679
C	6.18788092465487	9.88751295502185	1.19017435627986
C	3.14874678224857	16.42197996965031	7.17342263546953
C	2.43043753361854	17.31095129432856	3.15998272457415
H	1.50692419388322	16.75907388549244	3.05561728752782
C	9.69482892843718	10.18927274693945	3.49467652304075
C	0.14680808266866	14.36616690214194	3.58691233894206
H	0.52746525831281	13.50683705290425	3.05579034201566
C	6.86356986374876	9.34436332588345	8.84190793931612
C	2.91011916312956	17.70951049647613	6.70198330558455
H	3.47098008066324	18.06524960623636	5.84891127589423
C	6.87705019786591	8.13952685069439	5.95628657701473
H	6.16914294784943	7.60877474591261	6.57192726570567
C	5.40679150347946	14.42628683253676	1.74433176900517
H	5.84700043228149	15.41960779800106	1.66969006841125
H	5.64139435508390	13.87721200034649	0.82981197767233
H	5.86906284888119	13.91068346823444	2.58454329947777
C	8.80063510813710	9.55750937602083	5.74267285781121
H	9.58417197013521	10.14325441165655	6.19764888082229
C	6.78223302747597	8.03174455257164	4.56898785426828
C	2.41685523258908	15.95313315117355	8.27004983704438
H	2.58108825908257	14.94208274921662	8.61445864443216
C	3.16562475551180	9.74264879447347	1.50182369226471
C	7.05004011296039	9.34398473929242	10.23067818383438
H	6.22143197161333	9.60325718728352	10.87598778705908
C	0.63322691580432	14.64317999423792	4.87091133344802
C	1.46704945571148	16.75106744602103	8.89520293491377
C	4.11486502124060	8.53335331793117	7.57097597036552
C	-0.78861715235479	15.18910278309173	2.97706316677994
C	7.87267844366686	8.90769445964118	6.55632059636188
C	3.24014621951092	15.27689915164151	0.80344927493177
H	2.16367929350545	15.36540886603197	0.95763405580638
H	3.40988788437217	14.73331584914671	-0.12775805189189
H	3.65537020856908	16.27863076690019	0.69413137401813
C	9.89662476411216	11.58073326587798	3.60931865080698
C	5.47537634903697	15.55639122460500	7.23285023395631
C	0.14483481873738	15.75607570126715	5.54775395191922
H	0.51049370240931	15.96559553527423	6.54174507189506
C	8.62301023904156	14.76582156276891	2.78042824966128
H	8.17759161807123	13.99516755983440	2.16527854826257
C	9.20456388080056	8.72864005796054	8.62379882658006
H	10.04569157860672	8.47798235268016	7.98963815139126
C	7.96912106046290	9.00157008450791	8.03243364520913
C	6.94471739145799	11.05571967079915	1.31943615747991
H	6.73958909232275	11.74200808697671	2.12850709742422
C	8.72452803341266	9.47033879518912	4.35465306842089
C	8.58378737161285	12.49900816419516	7.57161232245381
H	7.52612307883676	12.38980609270353	7.38230349748462
C	9.47173535940740	12.65880495299605	6.50384893617340
C	4.82425267750965	17.31613264902924	3.42159356378951
H	5.74828175281276	16.76639380909667	3.53040656399923
C	-0.80967136877831	16.59346280850998	4.96283672774513
C	1.17919522923783	12.50689011803602	6.04717115911063
C	3.31585361440586	13.09635424357273	1.97733182131747
H	3.73434290766025	12.49998037635509	2.78085022384467
H	3.54703645206836	12.59641859542834	1.03858659388209
H	2.23374805075748	13.11682527271328	2.08864356025926
C	2.41517338142632	18.70742749279113	3.18361622414477
C	-1.26043948359061	16.30296890109724	3.68034340335854
H	-1.99267110011632	16.95347940428411	3.21422947675007

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H	7.68041070125388	8.59571045439882	2.70553391025893
C	5.71574933709832	7.19834654075456	3.96279975888433
C	10.85675103227502	12.16935248087399	2.77633346657875
H	11.02668063204534	11.23659303237218	2.83579344497030
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H	10.00806040884115	15.26904484803673	5.82317069105613
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C	6.56306064718677	15.35432144756376	6.18163212125513
H	6.40201903364966	14.45344622197107	5.59821690705716
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H	6.60162128159729	16.20350102243570	5.50028417858240
C	5.50521315314880	14.41728072547963	8.25023664060838
H	4.75448819601637	14.56925785433983	9.02440994042482
H	6.48288263886230	14.35861326106613	8.73335167006207
H	5.30431270121039	13.46480827678788	7.76468718236944
C	7.98907445772858	11.33421689821904	0.44618239576800
H	8.58283545017267	12.22876012667830	0.58166522838752
C	1.25919698639682	18.04587287588193	8.41069344402534
H	0.51620931720432	18.67739150864917	8.88680087678786
C	4.84722595985507	7.69244046309544	2.96612966796096
C	3.09706395834355	10.07826523285051	0.14620211137410
H	4.00910746731802	10.16864864380199	-0.43048745996429
C	4.86711022921580	11.90304068279969	10.22395261364419
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H	5.94858340899578	8.08380797551370	0.03492788598797
C	9.29225542920972	17.06283540908529	3.04461901620358
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H	10.75499101985863	12.49372452366478	10.17492364444580
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H	7.78378819767323	8.58494797596088	-1.52502372136328
C	1.97369261588636	18.53857119142272	7.32266077122707
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C	11.34696406541674	10.06721629112431	1.72493898219221
H	11.89111725128234	9.47987356262816	0.99563769853241
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H	-0.78889466319501	15.60766739297585	0.86643114610253
H	-2.33612202569791	15.03551125804243	1.48038148771934
H	-0.99362700979411	13.90170348232164	1.26127118739270
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H	3.44781405669184	9.52949542900037	5.78287541411621
C	1.87641587850601	10.32203813536030	-0.47578997827867
H	1.84854209744019	10.58617114761716	-1.52593215003045
C	1.11291771914480	19.44953079364586	3.04527664678217
H	0.62289136855138	19.20505749840016	2.09965201617860
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H	12.36059209248222	12.78414598944545	8.30893397421585
C	4.02075006639067	7.34285833026873	8.30141270104805
H	4.57835184858783	7.23286786564116	9.22530746553601
C	3.77829535049337	5.49777201903284	2.87663501640350
H	3.02811144436095	4.84619343988686	2.44564305800432
C	4.18959222711781	12.58338962304277	11.22734701394923
H	4.64441862794886	13.44646269514792	11.69791272895682
C	1.77459388361065	19.95147614725267	6.84278008376158
H	2.51944791067807	20.61753909945014	7.28864725801685
H	0.78972171340031	20.33185022693799	7.11691549052076
H	1.88706878030372	20.01979525503774	5.76135565553760
C	4.61852487246708	5.03601100592882	3.88021071735414
H	4.53174226635057	4.02036062859882	4.24571805080069
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C	6.12315897256997	19.45796635103268	3.65683564282384
H	6.05199146862340	20.15161734465265	4.49813823077874
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H	2.39246985482851	12.68691646259249	12.40465540639021
C	2.61069041818598	7.57583634497939	5.92215079739512
H	2.08058662569300	7.66394950189965	4.98271124565950
C	3.23734083137697	6.28542844302646	7.85333053663355
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C	2.34927431795968	11.05027547162637	11.01151174708449
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C	2.53280160159017	6.39986927559854	6.65841744333255
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H	-0.37000301887239	13.41244496870921	7.27830618426472
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H	1.95431249162802	12.90664936904647	8.03284013298516
C	1.28630647326274	11.40344260929960	4.99340376984070
H	0.62182448691438	11.59584137347583	4.15228094704637
H	1.02030050970680	10.43486672368517	5.42220687854997
H	2.30448746713084	11.34640241650279	4.61372457581365

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