Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Is a Transition metal-Silicon Quadruple Bond Viable?

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## Computational Details

Geometry optimization has been performed using M06-2X,[1] M11[2] and PBE[3] levels of density functional theory using def2-TZVP basis set. Harmonic vibrational frequency calculations were also performed at the same level of theory to understand the nature of stationary point. All these structures were found to be at their local minimum geometry. Single point multi-configurational complete-active-space-self-consistent-field (CASSCF) calculations were further performed on the M11 optimized geometries to verify the electronic configurations. The calculations used 12 electrons in 12 orbitals, i.e., CASSCF(12e,12o) for closed shell singlet and CASSCF(11e,12o) for the doublet ground state geometries of $H_3Si\text{-}Ru(CO)_3$ and $HSi{\equiv}Ru(CO)_3$ molecules. All these calculations were performed using GAUSSIAN16 suite of program.[4] The relaxed force constant calculations were performed using Compliance3.0.2 program.[5,6] Adaptive natural density partitioning (AdNDP)[7] analyses were performed using Multiwfn[8] on the M11 optimized geometries.

## References


(1) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215.

(2) R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.* 2011, **2**, 2810-2817.

(3) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

(4) Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

(5) K. Brandhorst and J. Grunenberg, *J. Chem. Phys*. 2010, **132**, 184101.

(6) K. Brandhorst and J. Grunenberg, J. *Chem. Soc. Rev*. 2008, **37**, 1558.

(7) D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys*. 2008, **10**, 5207.

(8) T. Lu, and F. Chen, *J. Comput. Chem.* 2012, **33**, 580.

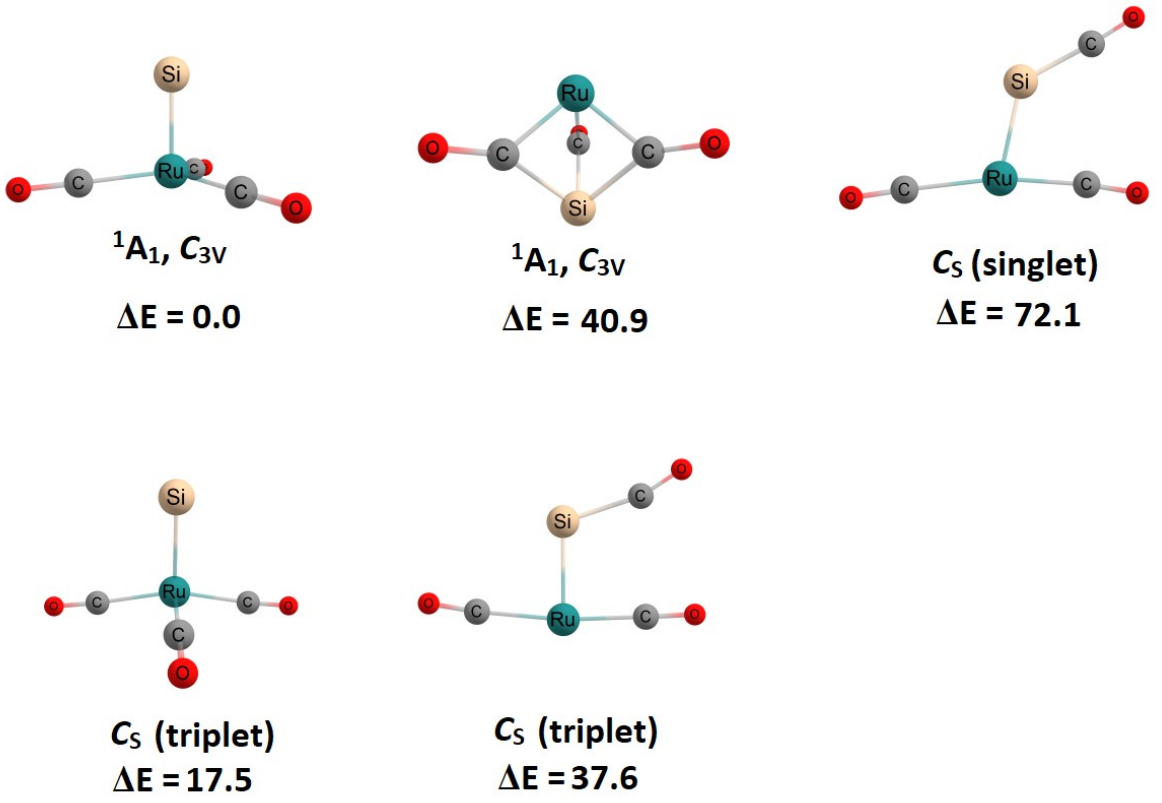


**Fig S1**. Relative energies (kcal/mol) of the isomers in their singlet and triplet states calculated at M11/def2-TZVP level.

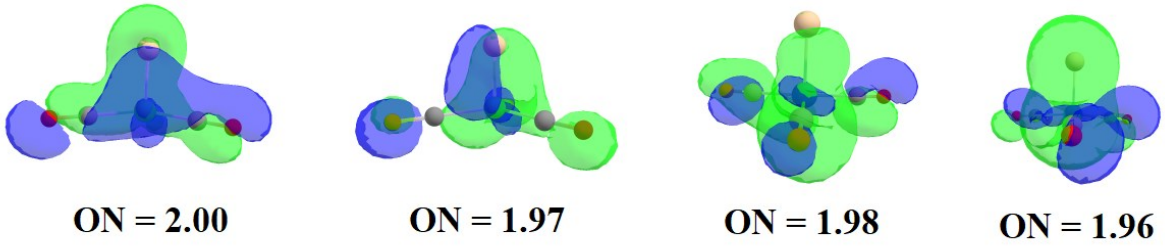


**Fig S2**. AdNDP orbitals showing 5c-2e bonds with their corresponding occupation number (ON).

Cartesian coordinates of the optimized geometries at different DFT functionals, lowest vibrational frequency along with the total energy in a.u.

**$SiRu(CO)_3$, $C_{3V}$, $^1A_1$ (M06-2X/def2-TZVP)**

**v1 = 27.5 $cm^{-1}$**

***Sum of electronic and zero-point Energies=  -724.294981***

***Sum of electronic and thermal Energies=  -724.284756***

***Sum of electronic and thermal Enthalpies=  -724.283812***

***Sum of electronic and thermal Free Energies=  -724.334660***

| | | | |
|---|---|---|---|
| 44 | 0.000398000 | 0.000156000 | -0.183401000 |
| 6 | 0.848982000 | -1.740312000 | -0.372978000 |
| 6 | 1.094802000 | 1.597787000 | -0.373101000 |
| 6 | -1.929941000 | 0.140779000 | -0.382056000 |
| 8 | 1.344718000 | -2.757222000 | -0.464778000 |
| 8 | 1.734289000 | 2.530906000 | -0.465961000 |
| 8 | -3.057249000 | 0.222950000 | -0.486888000 |
| 14 | -0.019617000 | 0.002180000 | 1.869961000 |

**$SiRu(CO)_3$, $C_{3V}$, $^1A_1$ (M11/def2-TZVP)**

**v1 = 58.5 $cm^{-1}$**

***Sum of electronic and zero-point Energies=  -724.291081***

***Sum of electronic and thermal Energies=  -724.281413***

***Sum of electronic and thermal Enthalpies=  -724.280469***

***Sum of electronic and thermal Free Energies=  -724.328540***

| | | | |
|---|---|---|---|
| 44 | 0.000208000 | 0.000009000 | -0.174863000 |
| 6 | -0.615754000 | 1.829494000 | -0.375203000 |
| 6 | -1.276011000 | -1.448242000 | -0.375626000 |
| 6 | 1.892734000 | -0.381046000 | -0.374449000 |

| | | | |
|---|---|---|---|
| 8 | -0.976060000 | 2.898443000 | -0.492508000 |
| 8 | -2.021775000 | -2.294579000 | -0.493055000 |
| 8 | 2.998610000 | -0.603694000 | -0.491430000 |
| 14 | -0.001511000 | -0.000213000 | 1.875828000 |

**$SiRu(CO)_3$, $C_{3V}$, $^1A_1$ (PBE/def2-TZVP)**

**v1 = 47.4 $cm^{-1}$**

***Sum of electronic and zero-point Energies= -724.068994***

***Sum of electronic and thermal Energies= -724.059192***

***Sum of electronic and thermal Enthalpies= -724.058248***

***Sum of electronic and thermal Free Energies= -724.107077***

| | | | |
|---|---|---|---|
| 44 | -0.000354000 | -0.000007000 | -0.164987000 |
| 6 | -0.861332000 | 1.714806000 | -0.388589000 |
| 6 | -1.062400000 | -1.598047000 | -0.389297000 |
| 6 | 1.914177000 | -0.115364000 | -0.396379000 |
| 8 | -1.369966000 | 2.727736000 | -0.516063000 |
| 8 | -1.689860000 | -2.541894000 | -0.517539000 |
| 8 | 3.044690000 | -0.183412000 | -0.532245000 |
| 14 | 0.013857000 | -0.001964000 | 1.916556000 |