

Cp*(ⁱPr₃P)Ru(Cl)(η²-HSiClMe₂): the first complex with simultaneous Si–H and RuCl⋯SiCl inter-ligand interactions†

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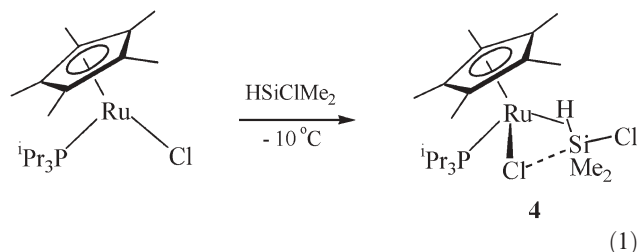
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The addition of HSiMe₂Cl to the unsaturated compound Cp*(ⁱPr₃P)RuCl gives an unstable adduct which, according to NMR ($J_{\text{H-Si}} = 33.5$ Hz), X-ray crystal structure and DFT evidence, is a silane σ -complex Cp*(ⁱPr₃P)Ru(Cl)(η²-HSiMe₂Cl) supported by an unprecedented, simultaneous inter-ligand RuCl⋯SiCl hypervalent interaction between the chloride ligand on ruthenium and the SiMe₂Cl group.

Non-classical inter-ligand interactions are formed by electron-deficient agostic and σ -complexes¹ and electron-rich hypervalent interactions (IHI).² Both of these types have been found for silyl groups,^{3,4} and we have recently shown how both IHIs and silane σ -complexes can be stabilised in the same Cp₂/PMe₃ ligand environment in titanocenes, depending on the substituents of the SiR₃ group.⁵ Complexes with several σ -bond ligands (H₂ and HSiR₃) are long known,^{1,6} but no examples with simultaneous interactions of both different types at the same metal centre have been documented so far. Here we report the synthesis and X-ray crystal structure of the complex Cp*(ⁱPr₃P)Ru(Cl)(η²-HSiMe₂Cl) which contains a stretched silane ligand, hypervalently interacting with the chloride ligand on ruthenium.

Complexes of type Cp*(ⁱPr₃P)Ru(Cl)(SiR₃)(H) (R₃ = Cl₂Me **1**, Cl₃ **2**, PhH₂ **3**, Ph(SiPhH₂)H), prepared by the reaction of Cp*(ⁱPr₃P)RuCl with silanes, have previously been reported as classical on the basis of their stability at room temperature and small Si–H coupling constants (<20 Hz^{3a}).^{7,8} In contrast, secondary silanes do not give stable adducts.⁹ We have found that complexes Cp*(R₃P)Ru(Cl)(HSiR₃) (R₃ = PhH₂ **3**, SiClMe₂ **4**, SiPhMe₂ **5**) have very different stabilities. While the reaction of Cp*(ⁱPr₃P)RuCl with excess H₃SiPh readily affords **3** along with some Cp*(ⁱPr₃P)Ru(SiH₂Ph)(H)₂, in the case of HSiClMe₂ and HSiPhMe₂ at room temperature the equilibrium is shifted towards Cp*(ⁱPr₃P)RuCl and free silane. However, the adduct **4** forms at –10 °C (eqn. (1)), whereas **5** is observed only at –90 °C. The ¹H NMR spectrum of **4** at –40 °C revealed a hydride signal at –9.65 ppm, flanked by ²⁹Si satellites with a coupling constant $J_{\text{H-Si}} = 33.5$ Hz, suggesting the presence of a Si–H σ -interaction. No ²⁹Si satellites could be seen for **3** at room temperature but a clear $J_{\text{H-Si}}$ coupling constant of 30 Hz was measured at –10 °C. For **5**, $J_{\text{H-Si}} = 32$ Hz at –90 °C. Surprisingly, both values are slightly lower than in **4**, in spite of the presence of more

electron-donating R-groups at Si in **5**. The formulation of **3–5** as σ -complexes is not surprising, if it is taken into account that: (i) in Cp*(R₃P)Ru(Cl)(SiR₃)(H) the Ru atom is in the high formal oxidation state IV,¹ (ii) an electron-withdrawing chloride ligand is present¹ and (iii) that σ -complexes occur for the isolable compounds [Cp*(Me₃P)₂Ru(η²-HSiCl₃)]⁺ and Cp*(PhⁱPr₂P)Ru(Cl)(η²-H₂).^{10,11}



The variation of $\nu_{\text{Ru-H}}$ in the IR spectra of compounds **1–4** with the nature of SiR₃ group provides further support for the non-classical nature of **4**. Namely, the Ru–H stretch shifts to shorter wave numbers along the series **2**: 2120 cm^{–1} > **1**: 2096 cm^{–1} > **3**: 2000–2050 cm^{–1} > **4**: 1916 cm^{–1}. Although IR spectroscopy has been less popular than NMR spectroscopy as a means for characterising silane σ -complexes, a red shift of the M–H stretch indicates the formation of such a complex.^{3d} For comparison, in the classical compound Cp*(pyr₃P)RuH₂(SiPhMe₂)¹² the Ru–H stretches are observed at much larger wave numbers (2085 and 2055 cm^{–1} vs. 1916 cm^{–1} in **4**).

In accord with the spectroscopic evidence of a σ -complex, the X-ray structure† of **4** (Fig. 1) revealed an elongated Ru–Si bond of 2.3982(7) Å compared to the 2.2950(5)–2.364 Å range found in related chlorosilyl complexes of ruthenium⁷ and marginally shorter than in classical Cp*(pyr₃P)RuH₂(SiPhMe₂) (2.4213(7) Å)¹² which has only donor groups at Si. In addition to the short Si⋯H contact of 2.05 Å, which is probably subject to the uncertainty of the hydride's location from the X-ray study, there is a short Si⋯Cl contact of 3.014 Å between the silyl and chloride ligands (the sum of the van der Waals radii is 3.81 Å).¹³ The Cl–Ru–Si–Cl torsion angle of 179.5° is close to 180° and the Cl–Si–Cl angle is 165.61°, signifying the relative *trans* disposition of the two Cl groups. There appears to be a donation from the Ru-bound chloride lone pair to the $\sigma^*_{\text{Si-Cl}}$ antibonding orbital of the silane, leading to a hypervalent silicon centre and the elongation of the Si–Cl(2) bond to 2.155(1) Å, a value beyond the range 2.094–2.149 Å typical of classical chlorosilyl complexes.^{7,14} However, the IHI of the type Ru–H⋯Si–Cl is missing in **4** since the Si-bound chlorine and hydride are not in a *trans* disposition.^{3d,4,5} In comparison, shorter Si–Cl (2.144 Å) and Si–Ru (2.364 Å) bonds are found in the

† Electronic Supplementary Information (ESI) available: Details of the preparation of **4** and DFT calculations of **7–10**. See <http://www.rsc.org/suppdata/cc/b5/b500679a/>

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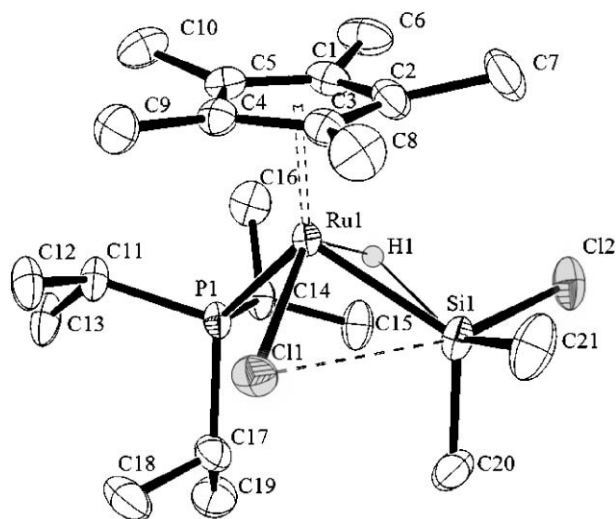
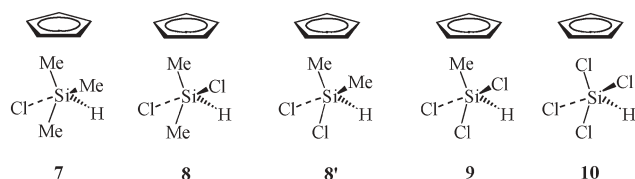


Fig. 1 Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Ru(1)–Si(1) 2.3982(7), Ru(1)–P(2) 2.3813(6), Ru(1)–Cl(1) 2.4129(6), Si(1)–Cl(2) 2.155(1), Si(1)–C(20) 1.872(3), Si(1)–C(21) 1.885(3), Si(1)–Cl(1) 3.014(1), Ru(1)–H(1) 1.53(3), Si(1)–H(1) 2.05(3); Si(1)–Ru(1)–P(1) 103.36(2), Si(1)–Ru(1)–Cl(1) 77.59(2), Cl(1)–Si(1)–C(20) 88.85(1), Cl(1)–Si(1)–C(21) 87.62(1), Cl(1)–Si(1)–Ru(1) 51.42(1), Cl(1)–Si(1)–H(1) 85.3(10), Cl(2)–Si(1)–H(1) 81.2(10), Cl(2)–Si(1)–Ru(1) 114.20(3), Cl(2)–Si(1)–C(20) 101.04(12), Cl(2)–Si(1)–C(21) 100.08(10), Ru(1)–Si(1)–C(20) 119.84(10), Ru(1)–Si(1)–C(21) 115.37(10), Cl(2)–Si(1)–Cl(1) 165.61(3).

classical complex Cp*(Ph₃P)RuH₂(SiClMe₂).¹⁴ It is also informative to compare the X-ray structure of **4** to that of closely related compound Cp*(Me¹Pr₂P)Ru(Cl)(SiCl₃)(H) **6**.⁷ The latter of these complexes is at a more advanced stage in the oxidative addition of the Si–H bond to the ruthenium, and has a shorter Ru–Si bond of 2.3152 (8) Å due to the presence of three electron-withdrawing chlorine groups on the silicon. In spite of this, the observed RuCl⋯Si distance of 3.111(1) Å in **6** is 0.097 Å longer than in **4**. This difference stems from a more acute Cl(1)–Ru–Si bond angle in **4** (**4**: 77.59(2)° vs. **6**: 82.26(3)°), clearly demonstrating the attraction in **4** between the chloride and silyl groups. Before this work, such an interaction between a chloride ligand and a main-group element was reported only for stannyl complexes in the form of MCl⋯SnCl inter-ligand bonding.¹⁵

To shed more light on the bonding arrangements in **1–6**, we used DFT§ to calculate a series of model complexes Cp(Me₃P)Ru(Cl)(SiCl_{*n*}Me_{3–*n*})(H) (*n* = 0: **7**, 1: **8**, 2: **9**, 3: **10**) and a rotamer of **8**, the complex **8'**, with a methyl group *trans* to the chloride ligand (Scheme 1). It can be seen from Table 1 that progressive substitution of the Me groups at Si in **7** for chlorine atoms leads to a shortening of the Ru–H and Ru–Si bonds and an increase in the Si–H separation due to increased back-donation



Scheme 1 Model complexes **7–10** drawn as Newman projections down the Si–Ru bond, so that the Ru atom is eclipsed and hence not visible.

Table 1 DFT-calculated bond lengths (Å), bond angles (°) and $J_{\text{H-Si}}$ (Hz) for model complexes **7–10**

	7	8^a	8'	9	10^b
Ru–H	1.613	1.604 [1.53]	1.602	1.603	1.598 [1.485]
Ru–Cl(1)	2.455	2.451 [2.413]	2.444	2.444	2.433 [2.416]
Ru–P	2.301	2.308 [2.381]	2.314	2.315	2.325 [2.323]
Ru–Si	2.474	2.427 [2.398]	2.426	2.388	2.361 [2.311]
Si⋯H	1.991	2.072 [2.054]	2.076	2.104	2.156 [2.092]
Si–Cl(2) ^c	—	2.168 [2.155]	—	2.148	2.129 [2.094]
Si–Cl	—	—	2.149	2.128	2.104/2.107
Si⋯Cl(1)	3.183	3.040 [3.014]	3.219	3.047	3.110 [3.102]
Cl(1)⋯Si–Cl(2)	—	161.4 [165.6]	97.8	162.4	162.0 [166.4]
$J_{\text{calcd}}^{\text{Si-H}}$	–23.0 [32] ^d	–19.5 [33.5] ^d	–17.3	–4.7	–0.4 [<6] ^d

^a X-ray data for **4** in brackets. ^b X-ray data for Cp*(¹Pr₂MeP)Ru(Cl)(SiCl₃)(H) in brackets. ^c The atom Cl(2) on Si is *trans* to the chloride ligand Cl(1). ^d $J_{\text{obs}}^{\text{Si-H}}$ for **5**, **4**, **1** and **2** in brackets.

from the metal to the $\sigma^*(\text{Si-H})$ antibonding orbital.¹ Noteworthily, the RuCl⋯Si contact distance decreases from **7** to **8** and then increases again from **8** to **10** as the Ru–Si bond shortens, whereas the rotation of the silyl in **8** to give **8'** results in an abrupt elongation of this contact and a decrease in the Si–Cl(2) bond length from 2.168 Å to 2.149 Å. Overall, the rotamer **8'** is 2.5 kcal mol^{–1} less stable than **8**. The rotation of the SiMe₂Cl group alone leads only to a negligible change in steric hindrance, since the second methyl group in both forms is directed towards the Cp ring. Furthermore, in accordance with the presence of the hypervalent interaction RuCl⋯Si–Cl, in complexes **7** and **9**, the Si–Cl bond *trans* to the chloride on Ru is longer than the Si–Cl bond *trans* to the Cp ring.

The progressive weakening of the Si–H interaction from **7** to **10** is mirrored by the decrease in absolute value of the calculated $J_{\text{H-Si}}$ (Table 1). The smaller absolute values of calculated $J_{\text{H-Si}}$ possibly reflect a greater degree of oxidative addition in model complexes **9** and **10**. Importantly, the sign of the coupling constant has been calculated† to be negative. The sign rather than the absolute value of $J_{\text{H-Si}}$ has been recently suggested to be a more rigorous criterion for the presence of a direct Si–H interaction.⁵

The large values of the Mayer bond orders¹⁵ (MBO, Table 2) and the overlap-weighted natural bond orders† unambiguously establish the presence of Si⋯H and Si⋯Cl interactions. The MBOs confirm the decrease in the Si⋯H interaction concurrent with the strengthening of the Ru–Si and Ru–H bonds from **7** to **10**. The rotation of the SiMe₂Cl ligand in **8** to give **8'** results in a somewhat more advanced Si–H addition and the loss of the hypervalent interaction Si⋯Cl(1) (the MBO for the Si⋯Cl(1) interaction decreases from 0.131 to 0.074, whereas the Si–Cl(2) bond strengthens from 0.876 to 0.915). Altogether, these data suggest the presence of simultaneous σ Si⋯H and hypervalent RuCl⋯Si–Cl interactions. The latter interaction is the strongest in complex **8**, the model of real compound **4**. In complex **10**, the model of real compound **2**, both interactions are weak.

Table 2 Mayer bond orders for 7–10, calculated from the DFT density matrix

	7	8	8'	9	10
Ru–H	0.684	0.701	0.711	0.708	0.722
Ru–Cl(1) ^a	0.707	0.691	0.734	0.718	0.757
Ru–P	0.806	0.805	0.796	0.791	0.781
Ru–Si	0.619	0.653	0.690	0.694	0.730
Si···H	0.172	0.157	0.149	0.143	0.125
Si–Cl(2)	—	0.876	0.915	0.919	0.962
Si–Cl'	—	—	—	0.983	1.013/1.028
Si···Cl(1)	0.095	0.131	0.074	0.122	0.101

^a Chloride ligand Cl(1) is in a *trans* position with respect to the atom Cl(2).

σ -Complexes with secondary Si–H interactions⁶ related to the *cis*-effect¹ have previously been reported and can alternatively be viewed as containing the distorted (R₃SiH₂)[−] moiety.² In 4, two different types of inter-ligand interactions occur simultaneously at the same metal centre—the residual σ -Si–H interaction and the unprecedented Cl···Si–Cl hypervalent interaction. The relative stabilities of 3, 4 and 5 show that the presence of the RuCl···Si–Cl interaction can stabilise the adduct, even for a tertiary silane. Interestingly, the values of $J_{\text{H-Si}}$ in 3–5 are very similar, in spite of the very different nature of their SiR₃ groups. Electron-withdrawing groups tend to decrease $J_{\text{H-Si}}$ in σ -complexes because of the increased back-donation from the metal onto the antibonding orbital $\sigma^*_{\text{Si-H}}$.^{1,3} Such an unusual trend in complexes 3–5 can be accounted for by steric factors. Namely, the increased repulsion of the larger tertiary silanes from the bulky Cp* ligand impedes the oxidative addition of the Si–H bond.

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Notes and references

† Selected X-ray data for 4: C₂₇H₅₀ClMoN₂P₂Si, $M_r = 526.58$, monoclinic, space group *P2₁/c*, $a = 10.9544(3)$, $b = 15.0911(4)$, $c = 15.4986(4)$ Å, $\beta = 99.898(1)^\circ$, $V = 2524.00(12)$ Å³, $Z = 4$, $T = 123.0(2)$ K, $\mu = 0.948$ mm^{−1}, $\rho_{\text{calcd}} = 1.386$ g cm^{−3}, $R = 0.0339$, $R_w = 0.0797$ for 6694 unique reflections with 239 variables. CCDC 261259. See <http://www.rsc.org/suppdata/cc/b5/b500679a/> for crystallographic data in CIF or other electronic format.

§ DFT calculations: All calculations were carried out using the Gaussian-03 package¹⁶ applying Becke's exchange functional¹⁸ in combination with Perdew's correlation functional (B-P86)¹⁹ and the Perdew–Burke–Ernzerhof exchange and correlation functionals (PBE–PBE).²⁰ The calculations were performed using the “Stuttgart” 28 electron effective core potential²¹ on the ruthenium atom, with a corresponding triple- ζ valence basis set augmented by one diffuse p function (contraction scheme

{31111/411/311}). On other atoms, the standard 6–31G** basis set was employed. Full geometry optimization for all the molecular structures was performed. The ¹H–²⁹Si spin–spin coupling constants for complexes 7–10 were calculated at B3LYP level using an extended basis set within the Gauge-Including Atomic Orbitals (GIAO) approach²² using the Gaussian-03 program.¹⁷ Natural bond orbital analysis was performed using the NBO 3.1 program,²³ incorporated in the Gaussian-03 package. The Kohn–Sham orbitals resulting from the DFT calculations were employed.

- 1 G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes*, Kluwer Academic/Plenum, New York, 2001.
- 2 G. I. Nikonov, *J. Organomet. Chem.*, 2001, **635**, 24.
- 3 (a) U. Schubert, *Adv. Organomet. Chem.*, 1990, **30**, 151; (b) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175; (c) Z. Lin, *Chem. Soc. Rev.*, 2002, **31**, 239; (d) G. I. Nikonov, *Adv. Organomet. Chem.*, in press.
- 4 (a) S. R. Dubberley, S. K. Ignatov, N. H. Rees, A. G. Razuvaev, P. Mountford and G. I. Nikonov, *J. Am. Chem. Soc.*, 2003, **125**, 644; (b) G. I. Nikonov, L. G. Kuzmina, S. F. Vyboishchikov, D. A. Lemenovskii and J. A. K. Howard, *Chem.–Eur. J.*, 1999, **5**, 2497.
- 5 S. K. Ignatov, R. B. Tyrrel, S. R. Dubberley, N. H. Rees, A. G. Razuvaev, P. Mountford and G. I. Nikonov, *Chem.–Eur. J.*, 2004, **10**, 4991.
- 6 K. Hussein, C. J. Marsden, J.-C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 1999, 1315.
- 7 A. L. Osipov, S. M. Gerdov, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *Organometallics*, 2005, **24**, 587.
- 8 (a) B. K. Campion, R. H. Heyn and T. D. Tilley, *Chem. Commun.*, 1988, 278; (b) B. K. Campion, R. H. Heyn and T. D. Tilley, *Chem. Commun.*, 1992, 1201.
- 9 P. B. Glazer and T. D. Tilley, *Organometallics*, 2004, **23**, 5799.
- 10 S. T. N. Freeman, F. R. Lemke and L. Brammer, *Organometallics*, 2002, **21**, 2030.
- 11 T. J. Johnson, P. S. Coan and K. Caulton, *Inorg. Chem.*, 1993, **32**, 4594.
- 12 V. Rodriguez, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1998, **17**, 3809.
- 13 J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991.
- 14 S. B. Duckett, L. G. Kuzmina and G. I. Nikonov, *Inorg. Chem. Commun.*, 2000, **3**, 126.
- 15 (a) M. Elder, W. A. G. Graham, D. Hall and R. Kummer, *J. Am. Chem. Soc.*, 1968, **90**, 2189; (b) T. Szymanska-Buzar, in *Ring Opening Metathesis Polymerisation and Related Chemistry*, ed. E. Khosravi and T. Szymanska-Buzar, Kluwer Academic, Dordrecht, 2002, pp. 349; (c) V. K. Bel'sky, A. N. Protsky, B. M. Bulychev and G. L. Solovechik, *J. Organomet. Chem.*, 1985, **280**, 45.
- 16 I. Mayer, *Chem. Phys. Lett.*, 1985, **97**, 117, addendum.
- 17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.01)*, Gaussian, Inc., Wallingford, CT, 2004.
- 18 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- 19 B. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822.
- 20 (a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
- 21 D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.
- 22 R. Ditchfield, *J. Chem. Phys.*, 1976, **65**, 3123.
- 23 E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, *NBO Version 3.1*.