

Molecule Matters

A Chromium Compound with a Quintuple Bond

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The first stable compound with a ‘quintuple bond’ reported recently is an exciting development that raises fundamental questions in theoretical and experimental chemistry.

The concept of single, double and triple bonds is deeply ingrained in the thinking of chemists. For example, we have a C–C single bond in ethane, a C=C double bond in ethene and a C≡C triple bond in ethyne. A single bond will have one electron pair, a double bond two electron pairs and a triple bond three electron pairs between the bonded atoms. For elements belonging to the second row of the periodic table, bonding involves primarily the *s* and *p* orbitals. Double and triple bonds have the so-called π -bonding (sideways overlap) in addition to σ -bonding (head-on overlap); single bond has one σ -bond, double bond is made up of a σ -bond and a π -bond, and triple bond consists of a σ -bond and two π -bonds. In the case of elements such as Si and P, belonging to third and higher rows of the periodic table, compounds with multiple bonds involving only *s* and *p* orbitals are, in general, not very stable, unless supported by sterically bulky groups. The first authentic *disilene* **1** (Figure 1) with a double bond between Si atoms was reported only in the year 1981 and the first *disilyne* **2** with a Si≡Si triple bond had to wait till 2004 [1]! In π -bonding involving heavier main group elements (such as Si, Ge, P, As), the extent of *d*-orbital participation is unclear but the current thinking discounts any significant *d*-orbital involvement even in a compound like triphenylphosphine oxide, Ph₃PO [2]. If this is true, chances of finding compounds of main group elements with bonds higher than triple are rather remote, because of the non-availability of suitable orbitals.

In contrast to the situation described above, triple and quadru-

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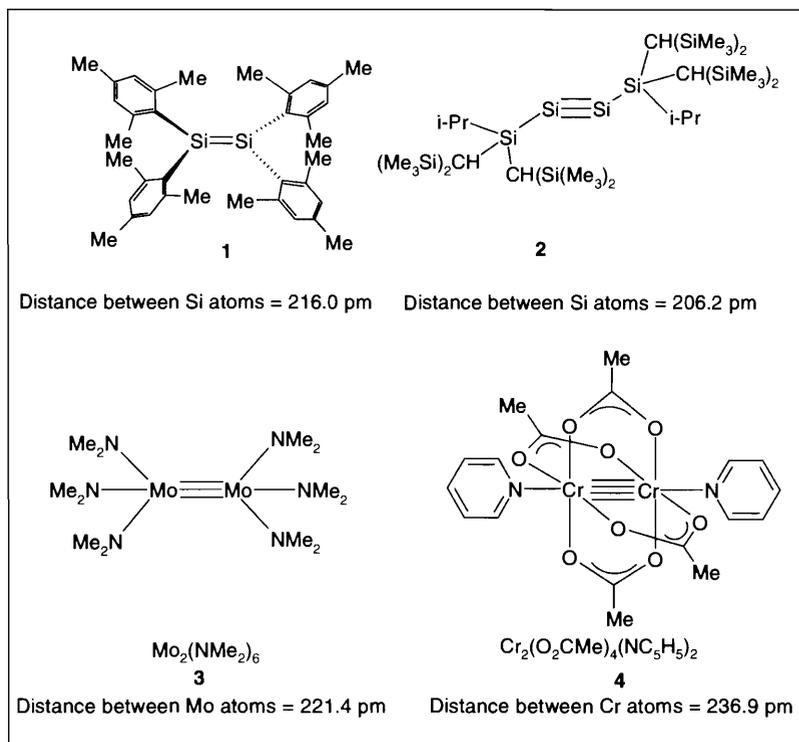


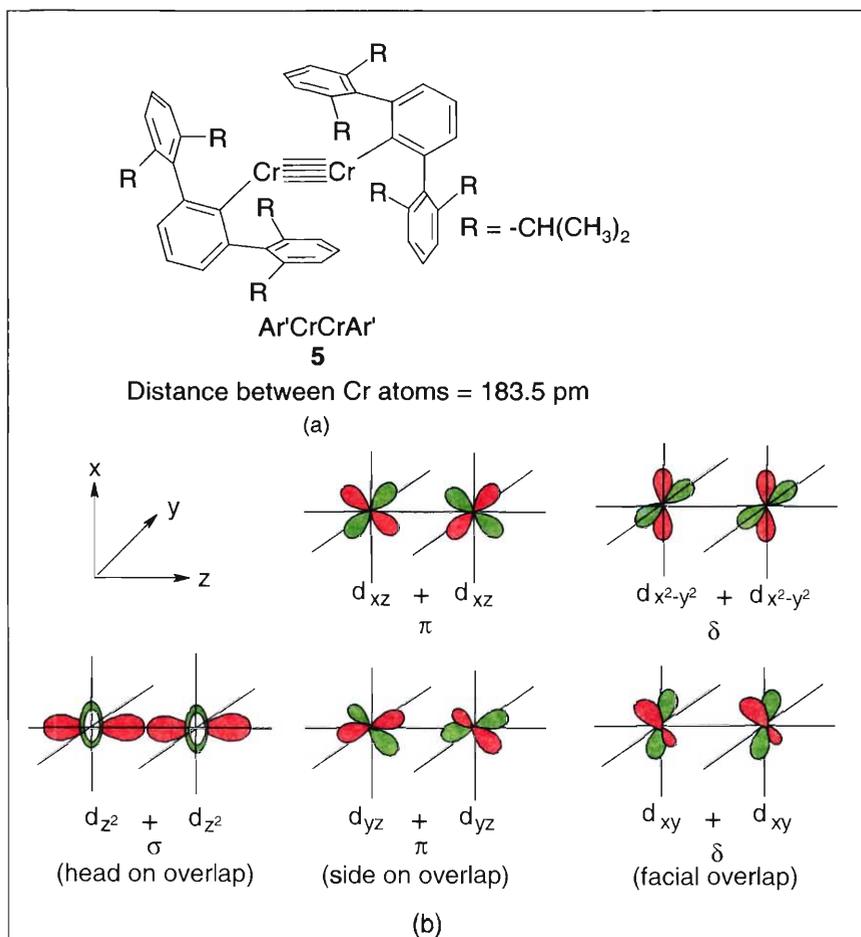
Figure 1. Molecular structures of compounds 1-4.

ple bonds involving *d*-orbitals can be found in many transition metal based compounds [3]. Compounds 3 and 4 represent two such examples (Figure 1). While 3 has a $\sigma^2\pi^4$ (6 electrons = 3 electron pairs; triple bond) configuration, 4 has a $\sigma^2\pi^4\delta^2$ (8 electrons = 4 electron pairs; quadruple bond) configuration; both involve the *d*-orbitals of the metal atoms (see also Figure 2). Thus the chromium atoms in 4 are held together by one σ , two π and one δ bonds.

Now, how about a *quintuple bond*, with *five* electron pairs between two metal atoms? This is what has been achieved recently by Philip Power and coworkers by using the bulky aryl group $C_6H_3-2,6-(C_6H_3-2,6-(i-Pr)_2)_2$ (labeled as Ar') that stabilizes the molecule 5 (Figure 2a) with chromium having a low coordination number [4,5]. This dark-red crystalline air-sensitive molecule is stable up to 200 °C. Each of the chromium atoms has six electrons and one of these is engaged in a bond with the phenyl carbon; thus the chromium is formally Cr(I). The remaining

five electrons from each chromium take part in the quintuple (fivefold) bond so that a total of ten electrons bind the two metal atoms together. The occupied molecular orbitals can be described as $\sigma^2\pi^4\delta^4$. The one σ , two π and two δ bonds between the two chromium atoms utilise d_{z^2} , (d_{yz} , d_{xz}) and ($d_{x^2-y^2}$, d_{xy}) sets of orbitals, respectively (Figure 2b). The fivefold bond in **5** is consistent with the extremely short distance of 183.5 pm between the chromium atoms (cf. 236.9 pm in compound **4**). At this point it is important to take note of the fact that a quintuple bond has been proposed for diatomic uranium (U_2) [6]; however, since the uranium atom has sixteen orbitals (seven 5f, five 6d, one 7s and three 7p) that are energetically close to one another, the bonding situation is considerably more complex.

Figure 2. (a) Molecular structure of **5**, and (b) Cr-Cr bonding interactions in **5**.



It is also significant to observe that the geometry of **5** is not linear; it is described as *trans*-bent, since the Cr-C bonds are oriented on opposite sides at an angle of $\sim 103^\circ$ with respect to the Cr-Cr bond [4a,4d]. A non-linear geometry was also found for the silicon compound **2**; note that the analogous carbon compounds, the normal alkynes, are linear. The expectation in both **2** and **5** was a linear geometry. These findings lead to exciting opportunities, for both theoretical and experimental chemists alike, to probe the mysteries of chemical bonding.

Suggested Reading

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