

## MAIN-GROUP CHEMISTRY

## Carbonyl trapped in silico



It took us a while to get our head around this but it is what makes bonding possible in the first place



When ligands bind to a transition metal its valence  $d$  shell gets split, which has interesting consequences if the shell is partially filled. Here, the energy differences between frontier orbitals can be small enough to make the metal a good  $\sigma$ -acid and  $\pi$ -base — useful properties when it comes to binding substrates such as  $H_2$  and CO. Chemists seek to replicate this behaviour using low-valent compounds of main-group elements, yet these species rarely have the appropriate atomic or electronic structure to afford stable adducts. A team led by Stephan Schulz and Peter Schreiner have hit back by preparing a silylene that enjoys steric and electronic protection in the form of bulky Ga-donor ligands. This privileged silylene, which the team now describes in

*Nature Chemistry*, is ideally set up to split  $H_2$  or form a rare complex with CO.

Carbenes are likened to transition metals because C has two valence electrons to distribute between an  $sp^2$  hybrid orbital and a higher-lying  $p$  orbital. A common strategy to stabilize a carbene is to introduce  $\pi$ -donor substituents that increase the singlet–triplet energy gap, but this often robs the carbene of its ability to activate certain bonds. Enter the silylenes — divalent Si analogues of carbenes that exist as singlet species yet have distinct reactivity.

Early matrix-isolation work on the simplest silylene,  $H_2Si$ , uncovered a non-planar  $H_2Si:CO$  complex in which Si plays the synergistic role of  $\sigma$ -acid and  $\pi$ -base reminiscent of transition metals. Schulz, Schreiner and their colleagues used density functional theory calculations to show that this complex is  $16 \text{ kcal mol}^{-1}$  lower in energy than the silaketene  $H_2Si=CO$ . By contrast,  $H_2C$  has greater access to its triplet state, such that its singly occupied  $sp^2$  and  $p$  orbitals engage in typical  $\sigma$  and  $\pi$  covalent bonding with CO to give ketene  $H_2C=CO$ , which now lies  $6 \text{ kcal mol}^{-1}$  lower than the non-planar isomer  $H_2C:CO$ .

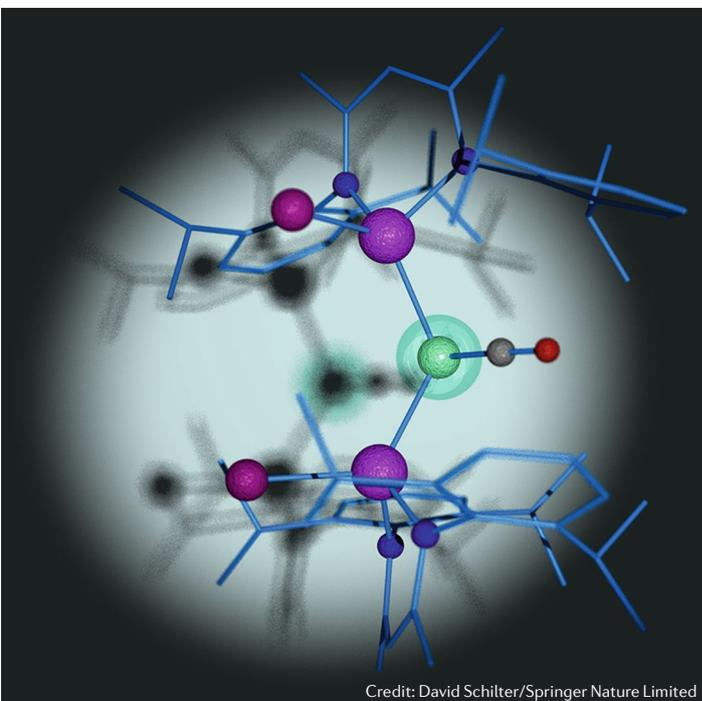
Despite its fragility, the observation of  $H_2Si:CO$  inspired the team to prepare a more stable analogue so they could probe its bonding and chemistry. For this they turned to other main-group chemistry they had developed, namely insertion reactions of unsaturated Ga species  $LGa$  ( $L^- = N, N'$ -bis(2,6-diisopropylphenyl)-1,3-pentanediiiminate). Thus, they converted  $SiBr_4$  to  $[L(Br)Ga]_2SiBr_2$ , a tetravalent species that undergoes

debromination when treated with a further equivalent of  $LGa$  to generate a putative  $[L(Br)Ga]_2Si$  intermediate. If left to its own devices, the Si centre inserts into a C–C bond of its own ligand, so Schulz, Schreiner and colleagues conducted debromination under CO in hopes of trapping it as a complex (when under  $H_2$  the reaction affords silane  $[L(Br)Ga]_2SiH_2$ ). Gratifyingly, the team isolated  $[L(Br)Ga]_2Si:CO$  and its X-ray structure reveals a non-planar arrangement that enables  $p_{Si} \leftarrow sp_C$   $\sigma$ -bonding and synergistic  $sp^2_{Si} \rightarrow \pi^*_{CO}$  backbonding. But the same arrangement exists in  $H_2Si:CO$ , so why is  $[L(Br)Ga]_2Si:CO$  stable at room temperature? Calculations on  $[L(Br)Ga]_2Si$  indicate that the bulkiness of the  $L(Br)Ga$  groups brings them apart and raises the energy of the  $sp^2_{Si}$  lone pair, which is now a better  $\pi$ -donor. Conversely, overlap of vacant  $p$  orbitals on the Si and Ga centres ensures that the  $p_{Si}$  orbital is a good  $\sigma$ -acceptor. Curiously,  $\pi$ -bonding dominates, so it is arguable if we can even call it ‘backbonding’. “It took us a while to get our head around this but it is what makes bonding possible in the first place,” notes Schreiner.

Like many a metal carbonyl,  $[L(Br)Ga]_2Si:CO$  undergoes substitution with isonitrile  $CNCy$  to give  $[L(Br)Ga]_2Si:CNcy$ . “I am pretty sure that the mechanism is associative because it proceeds at  $25^\circ C$  while the precursor is stable to decarbonylation up to  $80^\circ C$ ,” predicts Schulz. The team is now investigating ligand exchange and Si-assisted reactions at the CO ligand itself. This chemistry is a hallmark of transition metals and will no doubt motivate more investigations into such fertile main-group systems.

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