

## CO CAPTURE

# IL's a trap!

Carbon monoxide is a molecule of opposites. Although CO is toxic, even in small quantities, it is an important neurotransmitter that can trigger vasodilation and anti-inflammatory responses. CO is similarly ambivalent when it comes to its chemistry. The molecule has a small dipole moment, with the C atom bearing large HOMO and LUMO coefficients, such that it can act as both a nucleophile and an electrophile. Indeed, the character of the interactions between CO and other molecules can range from C being a pure  $\sigma$  donor, as it is in non-classical Cu<sup>I</sup> carbonyls, to situations in which C also accepts electron density through  $\pi$  backdonation or nucleophilic attack. With these interactions in mind, one can design systems that efficiently and reversibly capture CO, efforts which Sheng Dai and co-workers have made using carbanion-containing ionic liquids (ILs), as reported in *Angewandte Chemie International Edition*.

Many small molecules — including CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, NO and N<sub>2</sub>O — can be absorbed and transferred using ILs. The reversible capture of CO has proved more difficult because it

has a low polarity and the highest known bond dissociation energy. Previous studies have shown that approximately 0.0015 molar equivalents of CO can be stored in 1-butyl-3-methylimidazolium bistriflimide ([bmim][NTf<sub>2</sub>]) at ambient pressure; this value does not increase much at elevated pressures. The binding of CO — proposed by Dai's team to occur through a labile  $\pi$ -bound Tf<sub>2</sub>N<sup>-</sup>...CO complex — is rather weak. Others have also tried exploiting the  $\sigma$  donicity of CO by using Cu<sup>I</sup>Cl and 1-hexyl-3-methylimidazolium chloride mixtures, which can capture 0.020 equivalents of CO. The moisture sensitivity of the system and the propensity of Cu<sup>I</sup> to undergo disproportionation prompted Dai and colleagues to reconsider nucleophilic attack on CO. “We prepared carbanion-functionalized ILs with strongly nucleophilic anions in order to enhance the IL–CO interaction,” says Dai. The salts of choice were tetraalkylphosphonium  $\beta$ -diketonates, of which [P<sup>n</sup>Bu<sub>3</sub>Oct][acac] (where [acac]<sup>-</sup> is 2,4-pentanedionate) was the best performing, capturing 0.046 equivalents of CO at 25 °C and 1 bar (and 0.077 equivalents at 3 bar). This IL is an order of magnitude better at solubilizing CO than are imidazolium salts under similar conditions.

The higher affinity that CO has for [acac]<sup>-</sup> over [Tf<sub>2</sub>N]<sup>-</sup> could not be rationalized using density functional theory calculations when only non-covalent interactions were considered. The efficient binding of a gas must involve a significant negative enthalpy change to offset typical decreases in entropy. When [Tf<sub>2</sub>N]<sup>-</sup> binds CO in a side-on arrangement, the enthalpy change was calculated to be only  $-11.8 \text{ kJ mol}^{-1}$ . The binding of [acac]<sup>-</sup> to CO was predicted to be more exothermic ( $-77.6 \text{ kJ mol}^{-1}$ ) and is thought to involve insertion of CO into the central C–H bond of [acac]<sup>-</sup> to give [AcC(CHO)Ac]<sup>-</sup>, as evidenced by IR and NMR spectroscopy.

How well do the  $\beta$ -diketonates perform? They turn out to be quite robust, with the affinity of [P<sup>n</sup>Bu<sub>3</sub>Oct][acac] remaining constant over many CO binding (25 °C, 1 bar) and release cycles (80 °C, 0.1 bar). Their usefulness in solubilizing and transferring CO was demonstrated in the Pd(OAc)<sub>2</sub>-catalysed conversion of PhI, CO and <sup>n</sup>BuOH to PhC(O)O<sup>n</sup>Bu, for which [P<sup>n</sup>Bu<sub>3</sub>Et][acac] proved to be a superior catalyst compared to the typical bases (NEt<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub>). Dai attributes the observed doubling of reaction yields to cooperativity between the IL and Pd(OAc)<sub>2</sub>.

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Eventually, one would want to conduct such reactions not under an atmosphere of CO, but instead only using the CO trapped in an IL. The IL would be separated and recharged after the experiment, such that it represents a recyclable ‘CO-in-a-bottle’ material. This desirable situation will require stronger IL–CO binding. “We are also searching for new materials, such as deep eutectic solvents, that can selectively and efficiently capture CO at higher molar capacities (approaching 0.1 equivalents) and from mixtures of gases,” mentions Dai. Relevant to the environment and industry alike, CO capture and carbonylation are ubiquitous processes. The proposed CO transfer technology could make many of these processes safer and more efficient.

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