# Gas/Solid Reactivity of Unsaturated Ruthenium-Containing Molecular Solids

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One aspect of solid-state chemistry is the *reactivity* of a solid with small, mobile gaseous reagents. While reactivity *relies* on certain structural aspects of the solid, it transcends structure and thus reveals features of gas/solid permeability, and how this is influenced by solid structure and even by composition. We report here on gas/solid reactivity of *molecular* solids, where the packing is controlled mainly by the hydrocarbon periphery of the molecules. We choose to work with unsaturated (i.e., 16-valence electron) molecules, which allows our reactions to proceed under milder conditions than required for saturated molecules, where ligand dissociation appears to be a required preliminary step.[1] Results reported here involve the mildest reaction conditions yet reported for gas/solid reactions,[2] and are the first where authentic, structurally-characterized, unsaturated molecules form the molecular solid.

All reactions were carried out on microcrystalline samples at 25 °C (unless otherwise indicated) under 1 atm of gaseous reagent, and reaction progress was followed by visual color change, visible crystal fracture (due to volume expansion), solid-state IR spectroscopy, and (following removal of gaseous reagent) solution NMR spectroscopy. These reactions are not crystal-to-crystal transformations, but produce amorphous product.

$Ru(CO)_2L_2$ (L = P$^t$Bu$_2$Me), **I**, is a rare example of a persistent unsaturated Ru(0) molecule.[3] Its remarkable nonplanar structure is particularly adapted to (oxidative addition, **II**, and Lewis acid/base adduct, **III**) *product* geometry, which is expected to make
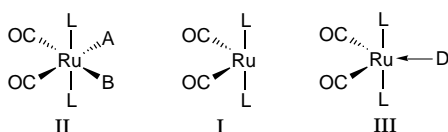


reactions especially facile (once the gaseous reagent reaches a four-coordinate Ru(0) site) in the solid state. The reactions in solution are all well-characterized, and generally occur during mixing. Reaction of red solid microcrystalline $Ru(CO)_2L_2$ with H$_2$, O$_2$, and Cl$_2$ occurs with significant bleaching to give *cis,-cis,trans*-Ru(H)$_2$(CO)$_2$L$_2$, $Ru(\eta^2$-O$_2)(CO)_2L_2$, and *cis,cis,trans*-RuCl$_2$(CO)$_2$L$_2$, respectively. Conversion is 25−100% complete in 24 h. These are the same products (and isomers) observed in the analogous reactions in solution. Reaction with HC≡CH is slower (90 h, 40% conversion), and gives the product of C−H

oxidative addition, *cis,trans*-RuH(CCH)(CO)$_2$L$_2$. We have not found, using solid-state IR spectroscopy, evidence for any Ru-($\eta^2$-HC≡CH)(CO)$_2$L$_2$ intermediate.

We anticipated that solid-state reactivity could permit detection of primary product when a secondary reaction of the primary product was possible. This expectation comes from both immobilization of the primary product molecule (inhibiting geometric isomerization) and the high ratio of metal reagent to reactant gas molecule within the solid lattice. In contrast to these expectations, $Ru(CO)_2L_2$ reacts with (two molecules of) HSiMe$_3$ to give yellow Ru(H)$_2$(CO)$_2$L$_2$ dissolved in liquid Me$_3$SiSiMe$_3$ (15 h, 100% conversion). At shorter reaction times, $Ru(CO)_2L_2$ and RuH$_2$(CO)$_2$L$_2$ are observed, together with a new compound, Ru(SiMe$_3$)$_2$(CO)$_2$L,[4] not detected in the reaction in solution.

The reaction of $Ru(CO)_2L_2$ with HCl is remarkably fast, being complete within 5 min at −78 °C. The primary product at this temperature is *cis,trans*-RuH(Cl)(CO)$_2$L$_2$, but this is rapidly transformed to *cis,cis,trans*-RuCl$_2$(CO)$_2$L$_2$ and H$_2$ by more HCl.

At the other extreme of rate is CO as a reactant. *Solution* calorimetry[5] shows this reaction to be among the most exothermic (−30 kcal/mol) of all fast (i.e., time of mixing) adduct formation and oxidative addition reactions we have studied,[6] but we find no correlation between thermodynamics and solid/gas kinetics. The *rate* of addition of CO to *solid* $Ru(CO)_2L_2$ is the slowest we have observed: 25% conversion after 150 h under 1 atm of CO at 25 °C, to give Ru(CO)$_3$L$_2$. We have therefore looked at the reaction of CO with solid, square-pyramidal Ru(H)Cl(CO)L$_2$,[7] a second unsaturated Ru species with "product geometry". Its reaction with CO is similarly slow: 42% conversion in 188 h to *cis,trans*-RuH(Cl)(CO)$_2$L$_2$.

Our current hypothesis is that the CO reaction is uniquely slow because the *size* of the product molecule with CO as the attacking reagent differs least from that of the reagent. This has the consequence of causing the least fracture of the reactive crystal in the case of CO. Consequently, the initial layer of product "passivates" the crystal surface against further reaction for CO as reagent, while those reagents whose product geometry stresses, then fractures the crystal lattice (e.g., oxidants, where an Ru−P bond lengthens by ∼0.1 Å)[8] thereby expose new reactive surface. This is analogous to corrosion of iron, whose oxide constantly flakes away, leading to massive, bulk oxidation, in contrast to aluminum, whose oxide coats the surface but does not flake away, leading to a protective coating (passivation).

Oxidation is not a *necessary* condition for faster reactivity, however. Ru(H)$_2$Cl$_2$(P$^i$Pr$_3$)$_2$, with a non-octahedral geometry poorly adapted to product structure (i.e., ∠P−Ru−P = 112°),[9] reacts with CO to give a mixture of *cis,cis,trans*-RuCl$_2$(CO)$_2$(P$^i$Pr$_3$)$_2$, by displacement of H$_2$, as well as RuHCl(CO)$_2$(P$^i$Pr$_3$)$_2$, by displacement of HCl, within 1 h. Thus, CO as a reagent and "simple" adduct formation are not universally slow. Any source of a large change in molecular volume accelerates the solid/gas reactivity studied here. A small volume change can lead to surface "passivation".

The implication of these observations is that these gas/solid reactions do not involve significant diffusion of gas *through*

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(2) In previous work, the conditions used were more severe: high temperatures (80 °C, ref 1a; 70 °C, ref 1c) and high pressures (4 atm or higher, ref 1c).

(3) (a) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995,** *117,* 8869. (b) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996,** *118,* 10189.

(4) Ru(SiMe$_3$)$_2$(CO)$_2$(P$^t$Bu$_2$Me): $^1$H NMR (C$_6$D$_6$, 300 MHz) δ 0.59 (s, 18H, SiMe$_3$), 0.77 (d, $J_{PH}$ = 13.2 Hz, 18H, P$^t$*Bu*Me), 1.02 (d, $J_{PH}$ = 6 Hz, 3H, P$^t$Bu$_2$*Me*). $^{31}$P{$^1$H} (C$_6$D$_6$, 121.4 MHz): δ 43.7 (s). IR (Nujol, cm$^{-1}$): 1915, 1854 ν(CO).

(5) Li, C.; Oliván, M.; Nolan, S. P.; Caulton, K. G. *Organometallics* In press.

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(8) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989,** S1.

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the solid lattice.  We are currently pursuing experiments to test this idea that the solid surface is the primary reaction site.

The reaction of microcrystalline RuH(Cl)(CO)L$_2$ with acetylene gas demonstrates another principle.  Since the open coordination site of the reagent complex is *trans* to the hydride, we thought that immobilization in the solid state might give a simple adduct (eq 1); this might be metastable with respect to

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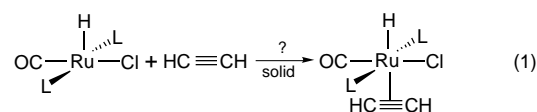
forming the $\eta^1$-vinyl product which is observed at the time of mixing upon reaction in solution (eq 2), due to the expected

(2)
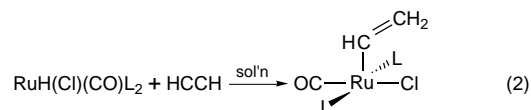
difficulty combining hydride and $\eta^2$-acetylene ligands which are not mutually *cis*.  In fact, the reaction proceeds to 56% completion after 101 h at 25 °C, and product identification by

solid-state IR spectroscopy shows only the $\nu$(CO) and $\nu$(C=C) bands of the $\eta^1$-vinyl product (i.e., eq 2 occurs).  There is no evidence for a "lattice-trapped" $\eta^2$-acetylene product.  This demonstrates the need for a fuller understanding of reactivity and/or mobility[10] in the solid state, to include either facile *cis/trans* isomerization in the solid state and/or attack of acetylene *cis* to the hydride ligand.

In summary, gas/solid reactivity (1) can be facile for a range of metal oxidation states (here 0, II, and IV), (2) is promoted by unsaturation, and (3) embraces adduct formation, oxidative addition, stimulated reductive elimination, and insertion reaction types.

**Supporting Information Available:**  Full experimental details of all reactions (3 pages).  See any current masthead page for ordering and Internet access instructions.

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