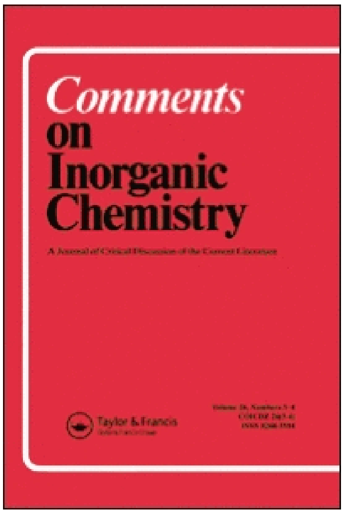

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STONES TO NANOPARTICLES...AND BEYOND

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STONES TO NANOPARTICLES . . . AND BEYOND

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MY INTRODUCTION TO ORGANO-TRANSITION METAL CHEMISTRY

I first met Gordon Stone in 1961, when he invited me over to Cambridge, Mass., for an interview. I wanted to change my research to the new and very exciting field of organometallic chemistry, and Gordon had a flourishing research group at Harvard that seemed the ideal place to learn about it. He and Judy made me and Marion most welcome and the four of us got on very well, aided by a delicious dinner featuring one of Judy's renowned Tamale pies. Gordon offered me, and I accepted, a Postdoctoral position until the following summer when he left Harvard to go back to England.

It was an excellent choice: Gordon was an inspiring teacher, both in the lecture theater and in the lab and had a lively group: Paul Treichel, Bruce King, Emily Pitcher, Warren Steele, Herb Kaesz, Ron Plowman, to name but a few, and I was rapidly inducted into thinking organometallic thoughts. As some of Gordon's work had been in boron chemistry and since I also had some experience in that topic I found communication easy. Previously, at Cornell, I had started a project on cyclobutadiene-palladium complexes, building on work by Malatesta's group in Milan as well as on results from the Blomquist group. Gordon encouraged me to continue that work and gave me the theoretical background I needed better to understand the so-called hydrocarbon

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"π-complexes".[1] In fact, Michael Dewar, my PhD supervisor, had originated the concept of π-olefin complexes in a classic paper in 1951; alas, he then lost interest in the topic and never expanded on it.

However, I was fascinated by organometallic π-complexes, an appeal that has lasted much of my working life: initially making some new ones, and then looking at their reactivity patterns, and their modes of decomposition. In late 1962, I set up on my own at McMaster University in Canada where I pursued these interests, and also the new field of organic reactions homogeneously catalyzed by soluble metal complexes. Most workers in that area used complexes bearing tertiary phosphines and similar ligands; we decided to try π-complexes as catalysts. That work proved fruitful and, together with excellent co-workers such as Marguerite Games, Jung Kang, Avi Efraty, Bob Bruce, and Hans Dietl, we developed some very interesting chemistry. That expanded further in 1972 when I returned to England to the Chair of Inorganic Chemistry at Sheffield University and Pamela Bailey added her superb X-ray crystallographic ability to our effort. Whereas before we had had to deduce by "sporting methods" the structures of the new complexes we made, with Pam's help we could now SEE what they were. And, a little later, when Brian Mann added his enormous skill at NMR spectroscopy to our group, our expertise matched that of any group in organometallic chemistry.

π-COMPLEXES AS CATALYSTS

One of our early successes was the synthesis and correct identification of pentamethylcyclopentadienyl complexes of rhodium and iridium, $[M_2(Cp^*)_2(Cl)_4]$ $\{M{=}Rh, Ir; Cp^* = \eta^5\text{-}C_5Me_5\}$.[2] These were very amenable compounds, largely air- and water-stable, but with excellent reactivities. We also found that they were good olefin hydrogenation catalysts.[3]

Most interesting was our observation that some could also hydrogenate benzene and other aromatics.[4] But that led to a major complication: many of those reactions turned out to be only poorly reproducible, and from the dark colors of the solutions after catalysis, we guessed that metallic particles had been formed and that we were dealing with reactions that were both homogeneously and heterogeneously catalyzed.[5,6] Andres Millan discovered the anomalies but, as the techniques to unravel such problems were then not available, he moved to a project on hydrosilylation, which he sailed through without difficulty.[7] It took many years before we fully understood what was going on, helped by work by Martin

Bennett (at ANU, Canberra) and new techniques devised by Rick Finke (at Colorado State), when it became clear that many organometallic compounds were simply precursors that decomposed to extremely active nano-particulate metallic catalysts.[8]

In the meantime, the homogeneous catalysis work of the Sheffield group went well and, together with my careful and diligent colleague Tony Haynes, and with help from BP Chemicals in Hull, we investigated and solved several mechanistic problems in rhodium- and iridium-catalyzed alcohol carbonylation.[9,10]

Our synthetic studies also continued and, with some brilliant work by Kiyoshi Isobe from Japan, Amelio Vazquez and Isabel Saez (both from Spain), and Isabel's husband Glenn Sunley, we synthesized an amazing series of complexes, in particular the deep red dinuclear dimethyl-di-μ-methylene $[Rh_2(Cp^*)_2(CH_2)_2(Me)_2]$ {I, $Cp^* = \eta^5\text{-}C_5Me_5$},[11,12] which we applied to a very different problem.

ORGANOMETALLIC MODEL REACTIONS AND THE HETEROGENEOUSLY CATALYZED HYDROGENATION OF CARBON MONOXIDE

The hydrogenation of carbon monoxide to linear alkenes (the Fischer-Tropsch Synthesis FTS), is a major industrial process integral to such current important industrial projects as making liquid hydrocarbons (e.g., diesel) for internal combustion engines. The fossil fuel (methane, coal, biomass, waste, etc.) is first *reformed* into a CO-H_2 mixture (*syngas*), which is then led over a metallic catalyst (Fe, Co, Ru or Rh) supported on an "inert" oxide (silica, alumina, etc.) in the FTS reaction.

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

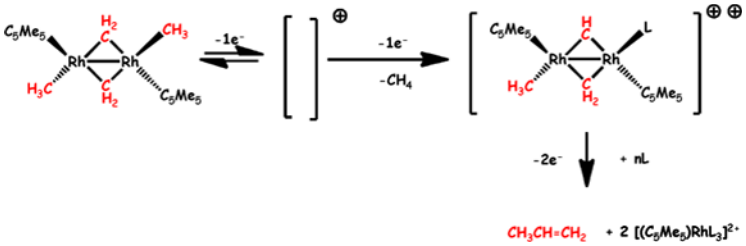
Despite several thousand patents and papers published on FTS, many aspects of the reaction, such as the mechanism, are still incompletely understood, a challenge that we could not resist. Therefore, parallel to the studies of model systems described below, Mike Turner, Helen Long, Nyoman Marsih, and Ruhksana Quyoum carried out detailed investigations of real FTS reactions over a variety of metal catalysts under "mild conditions" (1 atm, $^{12}CO{:}H_2$ 1:1: Ru/150°C, Co/180°C, Fe/220°C, or Rh/190°C;).[13] These were supplemented by ^{13}C labelling studies using $^{13}C_2H_4$ probes.[14]

The main products of the FTS are 1-n-alk*e*nes and methane; n-alk*a*nes are also formed but they largely arise from the alkenes in secondary reactions. Plotting the distribution of hydrocarbon products $\log(W/N)$ against N (where W is the weight fraction of products having carbon number N) gives a line very close to the theoretical Anderson-Schulz-Flory plot expected for a step-growth polymerization of C_1 species. Although the activities toward individual products differed somewhat, rather similar distributions and similar product labeling was found for all the catalysts, indicating an underlying similarity of mechanism. ^{13}C NMR analyses of the (crude) hydrocarbon products, showed that formation of the 1-alkenes occurred by a sequential regiospecific polymerization of C_1 species derived from CO when initiated by $^{13}C_2H_4$.[14]

A recurrent theme is the identification of the active C_1 species in FTS as a surface methylene, $CH_{2(ad)}$ or methylidyne, $CH_{(ad)}$. There is considerable agreement that the formation of such species occurs by adsorption of CO on the metal surface, M, followed by C-O cleavage assisted by spillover hydrogen (for full citations see references[14,18]). The initial product species is probably a surface carbide, $C_{(ad)}$, which is then sequentially hydrogenated to give surface methylidyne $CH_{(ad)}$, methylene $CH_{2(ad)}$, and methyl $CH_{3(ad)}$ and finally methane, CH_4, which desorbs as a major product.

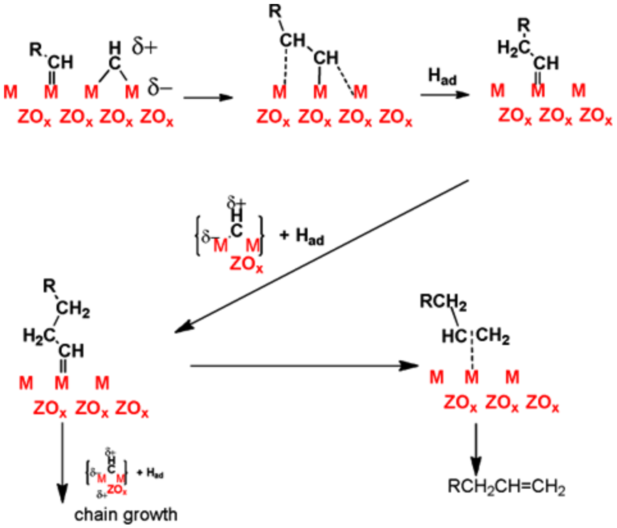
Many schemes have been proposed for the mechanism by which the polymerization occurs, but detailed examinations show serious shortcomings in most of them. We approached the problem via our discovery that the deep red di-methyl-di-μ-methylene complex (I) $[Rh_2(Cp^*)_2(CH_2)_2(Me)_2]$ was a most useful model for the $C + C + C$ coupling steps in the FTS. Although solid (I) is thermally stable to over 300°C, in the presence of 1-electron oxidizers (such as Fe(III), Ir(IV), etc.), it smoothly decomposed to give largely propene ($CH_2{=}CHMe$), methane, and $[Rh(Cp^*)L_3]^{2+}$ in solution. Extensive labelling studies combined with electrochemical measurements were consistent with a decomposition path (Scheme 1), showing that the propene arose from the coupling of three C_1 ligands (a methyl, a methylene, and a methylidyne) originally on the same molecule (I).[15,16]

We have combined the data from the model organometallic reactions and the heterogeneously catalyzed reactions into a more general mechanism for the FTS.[17,18] Previous suggestions for these polymerization mechanisms usually involved neutral surface species; however, this



Scheme 1. (Scheme appears in color online.)

ignores the fact that the interfaces between the metal and the oxide support, where the reaction takes place, are very polar. Furthermore many organic and organometallic reactions involve charged species. Thus we propose that the adsorbed methylidyne is electrophilic by charge polarization and readily couples first with a methylene (R=H) and then with an alkylidene at the interface, as represented diagrammatically (Scheme 2). This is somewhat analogous to the use of a very polar solvent to promote reactions of polar species in solution. In this symbolism M is the FTS active metal (Fe, Co, Ru, or Rh), and ZO_x is the oxide (typically silica, alumina, etc.) on which the metal M is deposited. This scheme fits the experimental data currently available, where FTS activity



Scheme 2. (Scheme appears in color online.)

is determined by the composition, size, and shape of the catalyst nanoparticles and their interaction with the support.

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It has been an exciting privilege to chart the progress from organometallic complexes and homogeneous catalysis initially inspired by Gordon to the new frontiers where inorganic, organic chemistry, catalysis and surface science meet. I thank all my coworkers and colleagues for their help without which the work would not have been possible.

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