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FROM SILICON-HYDROGEN TO CARBON-HYDROGEN ACTIVATION

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My doctoral research with Gordon Stone involved the study of diborane reactions in a Stock-type high vacuum system, complete with mercury float valves and a Sprengel pump [1]. It was an elegant way to investigate reactions, and when I began academic research at the University of Alberta in 1962 I set about building high vacuum systems to continue the investigation of volatile boranes. As events transpired, their use was of rather short duration.

Although Stone's involvement in transition metal organometallic chemistry did not begin until 1958 or so, my education in these matters had not been entirely neglected. The Wilkinson group was going at full throttle in metallocene chemistry when I was a graduate student at Harvard (1953–56). During the period 1957–62, when I was employed at Arthur D. Little, Inc., in Cambridge, Massachusetts, I was able to share vicariously in the excitement as the Stone group was entering the arena of organotransition metal chemistry. However, it was the pressure of presenting a course of 35 graduate lectures in 1964 that forced me to come seriously to grips with the transition metal side of organometallic chemistry, and I began to formulate some ideas for research in the field.

During that period I read a paper by R.D. Gorsich of Ethyl Corporation that particularly intrigued me [2]. It described the synthesis by straightforward metathetical reactions of compounds such as $(OC)_5MnPbPh_3$ and $(\eta\text{-}C_5H_5)(OC)_2FeSnPh_3$, and some of their reactions. These included a startling demonstration (eq. 1) of the robustness of one of these exotic covalent metal–metal bonds. The paper also drew attention to the important early work of Hieber and of Hein in Germany in this area.

$$Ph_3P(OC)_4MnSnPh_3 + 3Cl_2 \xrightarrow{25^\circ C,\ CCl_4} Ph_3P(OC)_4MnSnCl_3 + 3C_6H_5Cl \qquad (1)$$

I celebrated the end of the term that spring by cranking up one of the autoclaves in the Department and preparing a 10-gram batch of $Mn_2(CO)_{10}$ by the alkylaluminum method [3]. The compound was then commercially unavailable, and its synthesis was a reasonable test of skill and purpose. As a final year undergraduate research project, Helen Patil went on from there to prepare several new complexes having two different transition metals bonded to tin, and our initial paper in the area appeared early in 1965 [4]. This was an exciting field, and things seemed to

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move along much more quickly than in traditional boron hydride chemistry. The vacuum systems began to gather dust.

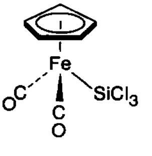
Our synthetic work at this time utilized mainly reactions of carbonylate anions in tetrahydrofuran solution with organic halides of germanium, tin and lead. In this straightforward way, for example, the stable series of compounds $(OC)_5MnEPh_3$ (E = Ge, Sn, Pb) was prepared and studied spectroscopically. Gorsich [2] had reported, and we confirmed, that the corresponding reaction of Ph_3SiCl with $NaMn(CO)_5$ in tetrahydrofuran led to extremely air sensitive scarlet crystals, utterly unlike the colorless, robust products formed using the Ge, Sn, or Pb analogs. We originally assumed, as did Gorsich, that the scarlet material was $(OC)_5MnSiPh_3$, but were troubled by the discontinuity at silicon in the fourth main group.

At about this time the work of Chalk and Harrod (then at the General Electric Company) on the facile reaction of organosilanes with $Co_2(CO)_8$ to form $(OC)_4CoSiR_3$ appeared [5]. Wally Jetz in my group tried a similar reaction with $Mn_2(CO)_{10}$ (eq. 2). Much more vigorous conditions were required, but the yield was

$$Ph_3SiH + Mn_2(CO)_{10} \xrightarrow[\text{sealed tube}]{160\text{–}165°C} (OC)_5MnSiPh_3 \tag{2}$$

reasonable and the authentic silylmanganese complex turned out to be just as robust as its analogs [6]. The red, air-sensitive product formed in tetrahydrofuran has since been shown to contain the anion $[Mn_3(CO)_{14}]^-$ [7], and the reaction of silyl-transition metal complexes with cyclic ethers has been investigated and turned to advantage [8].

It was clear to us after this experience that silicon hydrides had great potential as reagents. Trichlorosilane, for example, reacted with various dimeric metal carbonyls to afford trichlorosilyl derivatives [9]. A particularly interesting case was $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$. The reaction was investigated in detail by the meticulous Jetz, who isolated in addition to the expected **1** the very strongly acidic hydride **2**, and its salt **3** [10]. Our first intimation of this unexpected property of **2** came when we could not locate the high field proton resonance in acetone-d_6; it turned out that the complex was a 1/1 electrolyte in acetone owing to protonation of the solvent.



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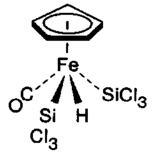

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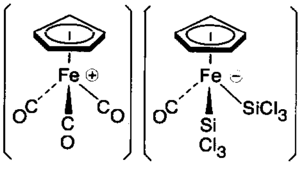

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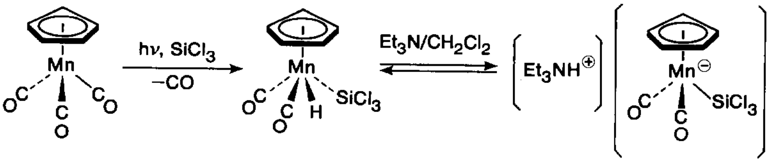
We soon discovered that photochemistry provided a powerful technique for synthesis of silyl hydrides, initially using mononuclear carbonyl complexes and trichlorosilane (eq. 3) [11,12]. Our interpretation was the conventional one of oxidative addition of the Si–H bond to a 16-electron intermediate generated by loss of carbon monoxide. The trichlorosilyl hydrides were weak acids, and could be deprotonated by bases such as triethylamine to form new and interesting anions (eq.



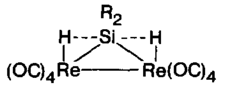
(3)

3) [13]. The acidity of transition metal silyl hydrides was influenced by the substituents on silicon. Thus the compound $(\eta\text{-}C_5H_5)(OC)_2Mn(H)(SiPh_3)$ (**4**), first prepared and studied by Jim Hoyano [14], did not react with triethylamine but underwent a smooth reaction with triphenylphosphine to form $(\eta\text{-}C_5H_5)(OC)_2Mn(PPh_3)$ with reductive elimination of the silane. Our detailed studies of this important reaction are described later.

For future reference we note that Jetz had prepared $(\eta\text{-}C_5H_5)(CO)Co(H)SiCl_3$ by the photochemical method, although in low (10%) yield [11,12]. At this time, Andy Oliver was the resident expert on rhodium and iridium, and was engaged in studies of reactions of $(\eta\text{-}C_5H_5)(OC)(PMe_2Ph)Rh$ and $(\eta\text{-}C_5H_5)(OC)(PPh_3)Ir$ that beautifully demonstrated their nucleophilicity [15,16]. I prevailed on him to extend our silane photochemistry to the metals below cobalt. From $(\eta\text{-}C_5H_5)(OC)_2Rh$, he obtained $(\eta\text{-}C_5H_5)(OC)Rh(H)SiR_3$ ($R = C_6H_5$ or $CH_2C_6H_5$) in low yield [17] but was unable to isolate any stable compounds from $(\eta\text{-}C_5H_5)(OC)_2Ir$. The irony of this failure will emerge later!

Our synthetic efforts on silicon and the heavier elements of the fourth main periodic group had provided a rather complete set of the series of six-coordinate complexes $(OC)_4M(ER_3)_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb; R = halogen, CH_3 or other organic group). Infrared studies of ^{13}CO exchange and ^1H and ^{13}C NMR spectroscopy showed that these complexes provided splendid examples of stereospecific ligand exchange processes [18] and fluxional behavior [19–22]. Several coworkers, particularly Roland Pomeroy and Liviu Vancea, carried this work forward. Its details, however, are not germane to this present account.

As an extension of our work with monohydridosilanes, Jim Hoyano explored the photochemistry of silyl dihydrides, R_2SiH_2, with metal carbonyls. Some of the novel products are shown (**5**–**10**) [14].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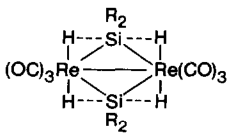
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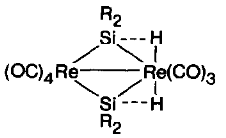
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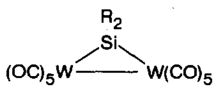
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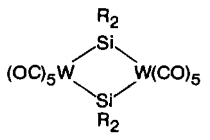
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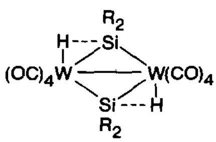
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Jim Hoyano's synthetic skills were augmented by the X-ray crystallographic group of my then colleague Mike Bennett, and several structures were done on these binuclear species: **5** [23], **6** [24], **7** [25], and **10** [26]. A vexing problem with these structures was our inability to locate the metal-bonded hydride ligands. Attempts were made to deduce their positions from those of the heavy atoms, but such arguments must be regarded as uncertain. All the hydride ligands in these complexes exhibit ^1H NMR values at very high field, indicative of bonding to a transition metal. Yet we were unable to observe in their infrared spectra any bands that could be assigned to terminal M–H or M–D stretching frequencies. For this reason we

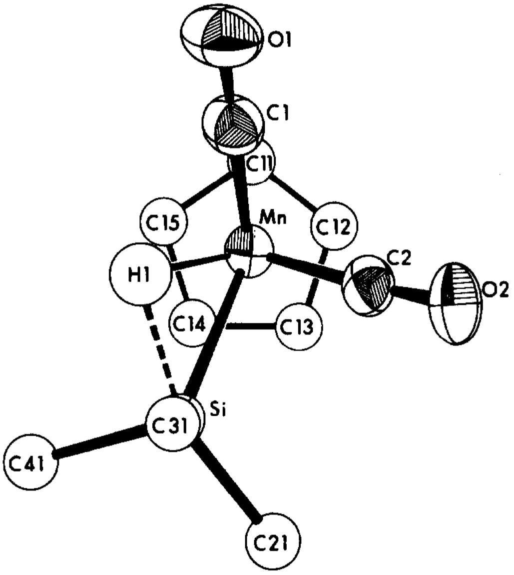


Fig. 1. The molecular structure of (η-C_5H_5)Mn(CO)$_2$(H)SiPh$_3$ (4). Selected bond lengths (Å) are: Mn–Si, 2.424(2); Mn–H(1), 1.55(4); Mn-C(1), 1.771(7); Mn–C(2), 1.764(7); average Mn–ring carbon, 2.140(4); Si–H(1), 1.76(4); average Si–phenyl carbon, 1.886(5). Selected bond angles (degrees) are: C(1)–Mn–C(2), 88.7(3); C(1)–Mn–H(1), 77(1); C(2)–Mn–Si, 80.4(2); Si–Mn–H(1), 46(2). For clarity, only the phenyl carbon atoms bonded to silicon are shown.

favored a bridging position between silicon and the metal, but the possibility remained that the hydride was in a terminal position with low infrared intensity. Herb Kaesz at UCLA had pioneered the use of Raman spectroscopy to address a similar problem for complexes such as $H_3Re_3(CO)_{12}$, and determined the Raman spectra of **4** and **5** (R = C_6H_5) and their deuterio derivatives. In his view, the results favored a M–H–Si interaction [27]. One datum which we felt supported Si–H interaction in **5** (R = CH_3) was the magnitude of J(H–Si–C–H) 1.5 Hz (cf. 4.2 Hz in free $H_2Si(CH_3)_2$) [23]. More recent work from the Bristol group, including location by X-ray methods of the hydride in question, indicates substantial Si–H interaction in a silylplatinum hydride [28]. Neutron diffraction structure determinations are sorely needed on representative dinuclear complexes of this type.

An X-ray structure that shaped our thinking was that of **4** (Fig. 1), determined by Bennett's group in 1970 [29]. The hydride ligand was reasonably well located, and clearly in a bridging position. The Si–H distance of 1.76(4) Å is about 20% longer than typical Si–H bonds in silanes (ca. 1.48 Å) [30] and much less than the sum of Van der Waal's radii for these atoms (3.30–3.45 Å) [31]. It is gratifying that a recent neutron diffraction study of an analogous compound shows closely similar structural features [32].

When Adam Hart-Davis arrived as a postdoctoral fellow with a background in kinetics, he found himself in the middle of our debate over the nature of the metal–silicon–hydrogen interaction in these compounds. With characteristic insight and enthusiasm, he began to do what one would expect a kineticist to do: measure rates. The reaction he chose to examine has been mentioned earlier: reductive elimination of Ph_3SiH from **4** in the presence of triphenylphosphine. Hart-Davis

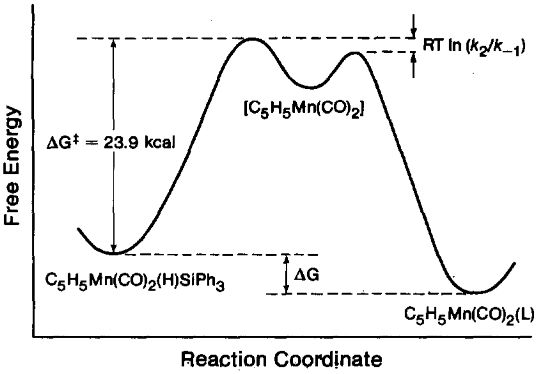
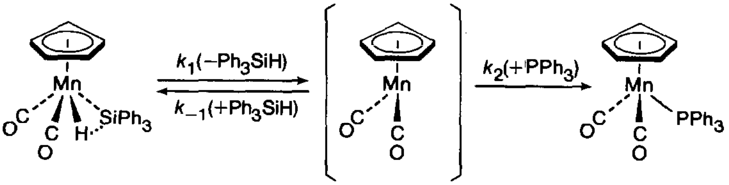


Fig. 2. Free energy profile for the reaction of equation 4 (L = PPh_3). At 50.1°C in n-hexane, $\Delta G^\ddagger$ 23.9 kcal and $RT\ \ln(k_2/k_{-1})$ 0.82 kcal. The value of ΔG is unknown but is certainly negative (as shown) since the reaction goes to completion. The profile is similar for L = CO, thus explaining why photolysis is required in the synthesis of **4**.

found that the reaction (eq. 4) involved a first order dissociation of Ph_3SiH from the complex to form an intermediate, for which Ph_3SiH and PPh_3 then competed [33].



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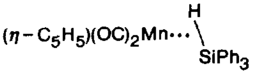
The ratio of these rates (k_2/k_{-1}) was 3.6, a surprisingly small value since Ph_3SiH is not normally regarded as a donor ligand; it presumably reflects the high reactivity and low selectivity of the intermediate. The free energy profile of the reaction is shown in Fig. 2.

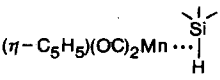
On the basis of the deuterium isotope effect on k_1, we pictured the activated complex in the reaction as having an almost completely formed H–$SiPh_3$ molecule, represented as **11**, with the angle made by the H–Si bond with the Mn · · · Si axis in the range 0 to 90°C.



$(\eta\text{-}C_5H_5)(OC)_2Mn\cdots\overset{H}{\underset{SiPh_3}{\diagdown}}$

11

Viewing the reaction as an oxidative addition (i.e., k_{-1}), Kaesz [27] made the valuable suggestion that the ground state structure of **4** should be regarded as having atom positions "arrested" along the reaction coordinate to full oxidative addition (**12**–**14**). In the case of **4**, a full separation of silicon and hydrogen (as in **14**) might



$(\eta\text{-}C_5H_5)(OC)_2Mn\cdots\overset{Si}{\underset{H}{|}}$

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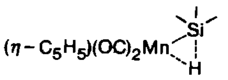
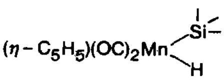


$(\eta\text{-}C_5H_5)(OC)_2Mn\overset{Si}{\underset{H}{\vdots}}$

13



$(\eta\text{-}C_5H_5)(OC)_2Mn\overset{Si}{\underset{H}{<}}$

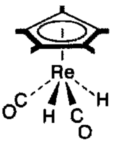
14

not be realized owing to steric crowding. I should also mention the extensive recent investigations of Corriu in this area, which are entirely consistent with Si–H interaction in compounds of this type [34].

While working with silylrhenium compounds, we had observed two instances of desilylation brought about by silicic acid. As the reader may suspect, these were accidental discoveries as a result of attempted chromatography, but one was of special importance because it converted **5** into the novel and interesting dimer $H_2Re_2(CO)_8$ [35]. The other case involved formation of traces of a complex of formula $(\eta\text{-}C_5H_5)(CO)_2ReH_2$ during silicic acid chromatography of $(\eta\text{-}C_5H_5)(OC)_2Re(H)SiR_3$ [36]. This pathway was later developed into a reasonable synthetic procedure for the new rhenium dihydride via eq. 5 [37].

$$\begin{tikzcd}
(\eta\text{-}C_5H_5)(OC)_3Re \arrow[r, "h\nu/Et_2SiH_2", "\text{heptane}"'] & (\eta\text{-}C_5H_5)(OC)_2Re(H)(SiHEt_2) \arrow[d, "\text{silicic acid}/CHCl_3"] \\
& (\eta\text{-}C_5H_5)(OC)_2ReH_2
\end{tikzcd} \qquad (5)$$

When we attempted to use $(\eta\text{-}C_5Me_5)(OC)_3Re$ in the sequence of eq. 5, yields of $(\eta\text{-}C_5Me_5)(OC)_2ReH_2$ (**15**) were very low, and other dinuclear rhenium complexes not containing silicon (**16** and **17**) [38] were formed. This led us to attempt an alternate and more direct synthesis of **15** by oxidative addition of H_2, which we carried out by ultraviolet irradiation of cyclohexane solutions of $(\eta\text{-}C_5Me_5)(OC)_3Re$ while purging with H_2. We termed this a "hydrogen mediated photolysis", and it worked, affording **15** in much improved yield [39].



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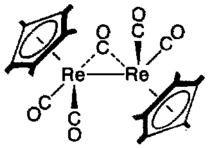

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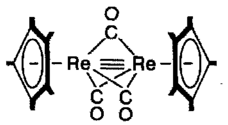

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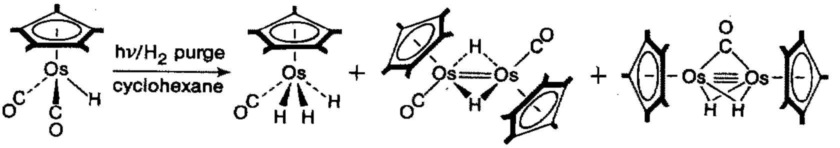
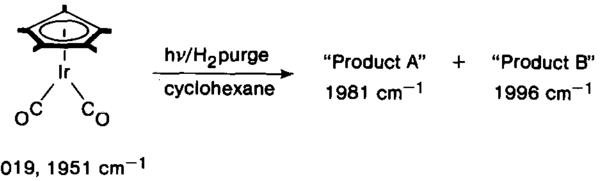
Since $(\eta\text{-}C_5Me_5)(OC)_2OsH$ was at hand from our work in osmium chemistry [40], we applied the hydrogen mediated photolysis to it with the results shown in eq. 6.



(6)

It appeared that this technique provided a new synthetic approach to hydride complexes, both anticipated and unanticipated. After rhenium and osmium, the next step was clearly iridium, and thanks to the work of Peter Maitlis during his Canadian period the required starting material $(\eta\text{-}C_5Me_5)(OC)_2Ir$ was well known [41]. We carried out the reaction with the results shown in eq. 7. The infrared spectrum after two hour's irradiation showed that about 50% of the starting material had reacted to form a new product or products with infrared carbonyl stretching bands at 1981 and 1996 cm^{-1} in an approximate 3/1 intensity ratio. The expected



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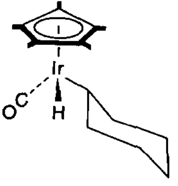
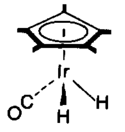
product, (η-C_5Me_5)(OC)IrH_2, should exhibit a single band. We repeated the experiment with an argon purge and observed only the new band of "product A" at 1981 cm^{-1}. Our supposition that oxidative addition of a solvent C–H bond had taken place was confirmed by conversion of "product A", (η-C_5Me_5)(OC)Ir(H)(C_6H_{11}), into its much more robust chloro derivative (η-C_5Me_5)(OC)Ir(Cl)(C_6H_{11}) for full characterization.

In fact, "product **B**" was the expected dihydridocarbonyl, subsequently prepared by an alternative route and fully characterized [42]. Formation of the dihydride was almost forgotten in the excitement over this explicit example of intermolecular activation of a saturated hydrocarbon. In retrospect, the experiment strikingly demonstrates the high relative reactivity of dihydrogen, since the molar ratio of H_2 to C–H bonds in the irradiated solution was about 1/29000!



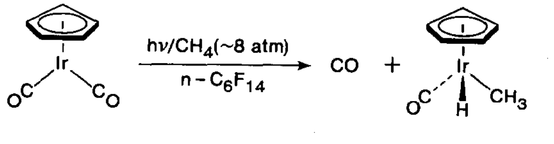
"Product A"



"Product B"

The manuscript of a communication on our discovery was mailed at the end of January 1982, two months after the initial discovery [43]. One week later, Chemical Engineering News [44] and the first 1982 issue of Journal of the American Chemical Society arrived in Edmonton and we learned of the results of Janowicz and Bergman [45] on their phosphine complex (η-C_5Me_5)(PMe_3)IrH_2. We had not been aware until then the prior work of Bob Crabtree [46] and of Hugh Felkin [47], which provided good indirect evidence for cycloalkane activation by iridium and rhenium complexes, respectively. Because his work involved the characterization of stable product complexes, we were familiar with Malcolm Green's key 1972 discovery of the insertion of tungstenocene into a benzene C–H bond [48], and his subsequent studies of this field.

We recognized that the simplest hydrocarbon, methane, was a substrate of special importance for C–H activation. Since all hydrocarbons we have examined react when irradiated with (η-C_5Me_5)$Ir(CO)_2$, the technical problem was to find an inert solvent. Perfluorohexane served this purpose and although the solubility of the complex was low, it was sufficient to demonstrate that activation occurred [49]. We found that the η-C_5H_5 analog was equally effective in methane activation (eq. 8), and subsequent work has shown that it is fully the equal of its pentamethyl analog as a C–H activator.

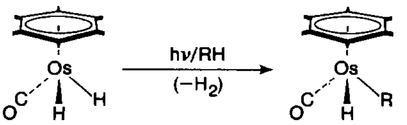


(8)

Throughout this C–H activation work we have assumed, as we did in the earlier Si–H reactions, that the photochemical part of the reaction involves CO loss to form a 16-electron intermediate, $(\eta\text{-}C_5R_5)(OC)Ir$ ($R = H, CH_3$). Following our methane results, we examined the substantial number of papers involving photochemistry of metal carbonyls at very low temperature in solid methane matrices. Three years earlier, Tony Rest had published a paper on matrix photochemistry of $(\eta\text{-}C_5H_5)(OC)_2Co$ [50], so I wrote to him suggesting a collaboration on the Rh and Ir analogs. The work at Southampton progressed rapidly, and at the XIth International Conference on Organometallic Chemistry in Calloway Gardens, Georgia, I had a look at some preliminary results. The infrared spectra showed unmistakably that $(\eta\text{-}C_5Me_5)(OC)_2Ir$ reacted upon irradiation in a dilute methane matrix at 12 K to form exactly the same hydridomethyl derivative we had produced at room temperature in perfluorohexane.

While this was certainly an interesting finding, it was disappointing as well. The earliest results seemed to imply that the intermediate was too reactive to observe even at 12 K. Fortunately, the more detailed studies that followed showed that this was not the case, although tracking the intermediates was not a simple task. About this time Roald Hoffmann and sent to us a preprint of his paper on C–H activation [51], so we were aware of his suggestion of an intermediate methane *complex* along the reaction pathway to full oxidative addition. Our results in methane and argon matrices have been substantially refined and extended since the initial communication [52], and we now consider that there is good evidence for low concentrations of a monocarbonyl methane complex (e.g., $(\eta\text{-}C_5R_5)(OC)M \cdot HCH_3$, as distinct from the "naked" monocarbonyl formed in an argon matrix) convertible by irradiation to the hydridomethyl compound [53].

Another direction our work has taken is the examination of the potential of other metals and other ligands towards alkane C–H activation (the conventional wisdom is that any species capable of inserting into an alkane C–H bond will also activate an aromatic C–H bond, but not vice versa). Our first successful step in this direction was taken by Bill Kiel, who was able to prepare the hexamethylbenzeneosmium complex **18** and use it in cyclohexane and neopentane activation (eq. 9, R = cyclohexyl or neopentyl) [54].



(9)

There is currently renewed interest in my group in the reactions of silanes with metal complexes in the belief that they will provide a useful model for some aspects of C–H activation. It is apparent that our early kinetic study of $(\eta\text{-}C_5H_5)(OC)_2Mn(H)SiPh_3$ (eq. 4) is of interest in relation to theoretical studies of the reaction of methane with $(\eta\text{-}C_5H_5)Rh(CO)$ [51]. Another reaction we have recently come upon is shown in eq. 10. This reaction goes to completion in the dark at room

$$(\eta\text{-}C_9H_7)(OC)_2Ir + R_3SiH \xrightarrow[-CO]{\text{n-hexane}} (\eta\text{-}C_9H_7)(OC)Ir(H)SiR_3 \qquad (10)$$

temperature and has been shown kinetically to be associative [55]. Facile $\eta^5 \rightarrow \eta^3$ conversion of the indenyl ligand is certainly involved. Here is a model that we would like a C–H bond to emulate! Unfortunately, because of less favorable thermodynamics, it is not likely to do so to an observable extent in this system. Nevertheless, we should be able to reach conclusions from the Si–H model about such important matters as the role of steric effects on the strengths of bonds to transition metals.

Conclusion and perspective

I referred earlier to an unsuccessful attempt by Andy Oliver to prepare (η-C_5H_5)(OC)Ir(H)$SiPh_3$ by irradiation of (η-C_5H_5)$(OC)_2$Ir and $HSiPh_3$ in benzene; that was in 1970. In the last experiment described in his notebooks (no doubt a little hurried due to his departure for a postdoctoral fellowship with Mike Lappert), he irradiated (η-C_5H_5)$(OC)_2$Ir in cyclohexane without triphenylsilane, presumably expecting dinuclear and trinuclear products analogous to those formed in the rhodium case. A few months later, Bob Stewart gave the silyl hydride preparation another try in n-heptane. Why did we not come upon C–H activation in 1970? From the weak infrared bands mentioned in the old research notebooks there is no question that we did, but without recognizing it or pursuing it. Our methodology called for the isolation of pure products from reactions, and the expected products would not have been nearly as sensitive as the aryl, alkyl, or cycloalkyl hydrides of iridium later turned out to be. The difficulty of working with (η-C_5H_5)(OC)-Ir(H)C_6H_5 is clear from a paper by Marv Rausch, who later made a more deliberate study of the photochemistry of (η-C_5H_5)$(OC)_2$Ir in benzene [56]. Above all, however, these events bear out Pasteur's dictum that "In the fields of observation, chance favors only the mind that is prepared." My mind was certainly not prepared for such a thing in 1970. Unfortunately I had not been following the homogeneous catalysis literature two years earlier when Jack Halpern asserted that the activation of C–H bonds, particularly in saturated hydrocarbons, was one of the most important and challenging problems in the whole field [57].

The title of this article notwithstanding, it never occurred to me during our work with silanes to use the word "activation", a terminology which is ubiquitous today. My interests were focussed on the structure and properties of the new complexes, and matters such as hydrosilation seemed in the province of organic chemistry. While distinctive organic and inorganic approaches to organometallic chemistry remain, there is now much greater overlap, to the benefit of the science. This has been driven home to me by the fine work of Bob Bergman, whom I had not met until we both found ourselves activating C–H bonds. Interaction with him has happily been both stimulating and pleasant, a situation that does not always prevail in such circumstances.

Quite clearly my journey from metal-metal bonds to Si–H reactions through H–H addition to C–H activation was not propelled by any master plan. It was possible because the support of my research was not contingent upon reaching a specific goal, leaving me with complete freedom to pursue what I judged to be most interesting and important.

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I have been privileged to have many talented and enthusiastic coworkers since 1962; unfortunately I cannot name them all or cite their work in this short account. I acknowledge the role of Professor Harry E. Gunning in organizing a Chemistry Department at the University of Alberta where the atmosphere and facilities for research are unsurpassed, and in hiring me!

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