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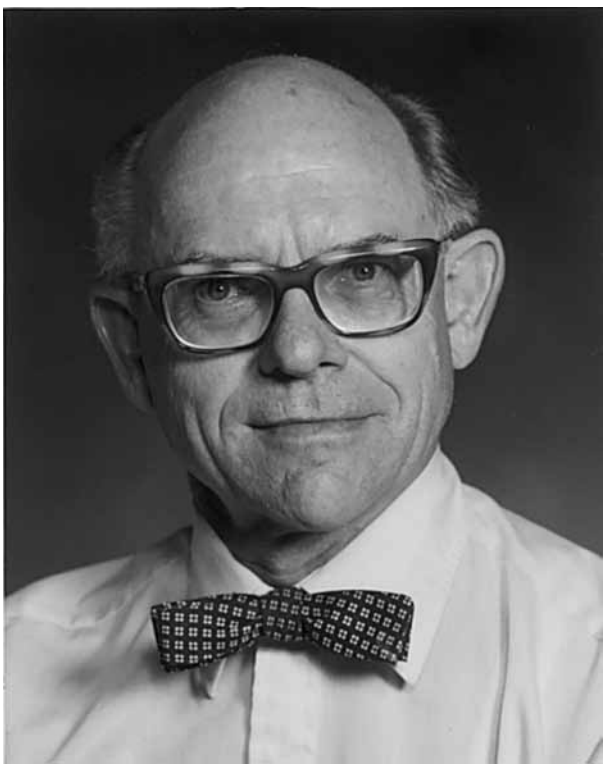
Foreword



Professor Frank Albert Cotton

As Larry Falvello pointed out to me on a recent trip to Spain, the importance of the work of F.A. Cotton in organometallic chemistry is much like the forgotten success of the late baseball great Joe DiMaggio. DiMaggio had an unbelievable hitting streak of 56 straight games. This is like Al's record of well over 1000 research contributions to our understanding of inorganic and coordination chemistry, including his singular work in metal–metal bonding. But just as we tend to forget that DiMaggio hit safely in an additional 17 straight games after missing in only one, i.e. hits in 73 out of 74 games, Al has published more than 250 papers in organometallic chemistry, with over 60 more in metal carbonyl chemistry, including the one in this volume. Sometimes we forget his impact on this sub-field. What a record!

Al Cotton started his Ph.D. studies with Geoffrey Wilkinson at Harvard in the early 1950s when ferrocene became the fuse that caused the explosion in the field. Al's thesis (1955) entitled 'Studies in Bis-Cyclopentadienyl Metal Compounds' appeared only four years after the preparation of the iron compound by Kealy and Pauson and only three years after the classic paper by Wilkinson, Rosenblum, Whiting and Woodward that actually caused the explosion. As Jack Dunitz has beautifully pointed out, this was an incredible leap in the understanding of bonding and structure in the field. Already in 1952, Cotton and Wilkinson published a paper on the heat of formation of this new aromatic molecule and Al contributed to nine more papers from the Wilkinson group over the next two years on this general topic. By 1955 Al had positioned himself to be the sole author of the first definitive *Chemical Reviews* paper on *Alkyls and Aryls of the Transition Metals*. I have often used a table from this review to introduce students to the fact that many of these elements, which today are known to have abundant alkyl and aryl chemistry, showed

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no evidence then of their future importance. The first paper in volume 1 (1959) of *Progress in Inorganic Chemistry* is a 124 page review of metal cyclopentadienyl chemistry which Al co-authored with Wilkinson. Of course, Al was the first editor of this very successful series now in its 45th volume.

Cotton has contributed many landmark papers that have changed the organometallic field forever. Fluxionality, a concept in stereochemical nonrigidity, an essential part of organometallic chemistry and catalysis, was attributable to Cotton in the main, through a series of papers and reviews he published in the mid 1960s. The seminal paper on $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ was the first in which NMR lineshapes were used to determine the mechanism and not merely the rate of the unimolecular rearrangements. In parallel with this work, Cotton and his students discovered and broadly explored fluxionality in metal carbonyls. Virtually every type of structural dynamics that metal carbonyls undergo was elucidated. This work led to the concept of the semi-bridging of CO and the opening and closing of CO bridges. Since infrared spectroscopy was an ideal tool for characterizing metal carbonyls because of the relatively easily recognized CO vibrations, Cotton, using a group theoretical formalism, developed a practical scheme for determining π-acceptor strengths and structural correlations.

Out of these structural and dynamic concepts of fluxional organometallics and metal carbonyls was born the important observation of a three-centered, two-electron bond encompassing C–H···M interactions. This bonding was first found in 1974 with the H-atom of the β-carbon of an ethyl group in an organometallic Mo complex, thought initially to be a 16-electron species. The Mo–H contact was about 2.20 Å so that the interaction, now generally referred to as agostic, effectively furnished the needed electrons to produce the closed-shell configuration. The strength of this agostic interaction was estimated using NMR results to be 17–20 kcal mol^{-1}, which Cotton subsequently showed was competitive with olefin–metal bonding. Where would modern cyclopentadienyl-based olefin catalysis be today without this insight?

There are numerous other Cotton firsts in the organometallic field. For example, the observation that molecules such as the $\eta^5\text{-}C_5H_5M(CO)_x$ type are aromatic like ferrocene was made by Cotton along with two other laboratories in 1958, the same year that Cotton and Waugh first observed the ^{13}C-NMR spectrum of a metal carbonyl, $Fe(CO)_5$. The ability of ethylene to coordinate *between* two metal atoms to form μ-bonds was first demonstrated in 1987 and again in 1990. These results have considerable importance for understanding bimetallic olefin catalysis. The first structural characterizations of the homoleptic quadruply bonded dinuclear alkyl compounds, $[Mo_2(CH_3)_8]^{4-}$ and $[Re_2(CH_3)_8]^{2-}$, also came from Al's studies. These compounds, with their absence of any M-ligand π-bonding, helped to define clearly the delta bond and its spectroscopy. Since Al always has been interested in the use of language to define chemical concepts, it is not surprising that the *hapto* notation, which is now universal in organometallic chemistry, was one of his many originals.

Al Cotton continues to make hits in organometallic chemistry. As recently as 1998 he described an organometallic route to the first titanium metal atom cluster compound. The new 6th edition of his *Advanced Inorganic Chemistry* (with Wilkinson, Murillo and Bochmann) has about 10% of its coverage devoted to organometallic chemistry and catalysis. Given the current litigation regarding patents in organometallic chemistry and catalysis, is it surprising that Al has come to know the finest restaurants throughout the country wherein Federal courts are located? As a lawyer in a major firm once told me, Cotton is the number one expert witness that the lawyers would like to have on their side in any patent case involving inorganic or organometallic chemistry. Through his use of both theory and experiment, Cotton has no peers when it comes to the impact of his chemistry upon the foundations of organometallic chemistry. It is a pleasure to honor him on his 70th birthday with this volume of the *Journal of Organometallic Chemistry*.

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