

This Week's Citation Classic

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Parshall G W. Intramolecular aromatic substitution in transition metal complexes. *Account. Chem. Res.* 3:139-44, 1970.
[Central Research Dept., Experimental Station, E.I. du Pont de Nemours & Co., Wilmington, DE]

Aryl amines and phosphines coordinated to transition metal ions often undergo a cyclization reaction in which an *ortho* C—H bond reacts with the metal to form a C—M bond. The review identified this chemistry as an emerging area with broad potential in synthesis and catalysis. [The SCJ® indicates that this paper has been cited in over 275 publications since 1970.]

G.W. Parshall
Central Research & Development
Department
E.I. du Pont de Nemours & Co., Inc.
Experimental Station
Wilmington, DE 19898

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"In the late-1960s, there was an explosion of reports about the involvement of ligand C—H bonds in reactions of transition metal complexes. Within five years, about two dozen reports appeared, mostly observations of cyclometalations in which *ortho* positions of aromatic ligands were coupled to the central metal ion of the complex. In addition to the published data, our work at Du Pont produced many other observations of this phenomenon.

"Despite the many publications on cyclometalation reactions, there seemed to be little general recognition of their scope or potential. The review was written to call attention to the area. I chose *Accounts of Chemical Research* as a medium for the review because it has a large and varied read-

ership. Its format was well suited to a discussion of the new work in our group.

"Our entry into this chemistry was unplanned. Robert Schunn was studying the catalytic isomerization of olefins. In order to discern the role of M—H addition to the olefin C=C function, he tried an experiment in the presence of deuterium gas. A surprisingly large amount of exchange occurred between D₂ and the organic C—H bonds in the system. By some thorough work, he showed the involvement of the *ortho* C—H bonds of the complex. Shortly thereafter, I found unexpectedly that the D₂ underwent extensive exchange with the *ortho* C—H bonds of the triphenylphosphine ligands of a cobalt complex of molecular nitrogen.

"Schunn and I had found catalytic processes in which the metal substituted the *ortho* C—H on the aromatic ring and was then replaced by deuterium. With this discovery, we had a tool to look for *ortho* C—H interactions in a variety of catalytic systems.

"In the review article, I forecast that this phenomenon would be widespread and would also extend to intermolecular reactions. These homogeneous catalytic C—H activation phenomena became a major field of study at Du Pont and elsewhere.¹⁻³ Partly as a result of this work, I was recently designated to receive the American Chemical Society Award in Inorganic Chemistry.

"Hundreds of examples of cyclometalation have been reported in the past 15 years. Reviews much more comprehensive than the *Accounts of Chemical Research* article are now available.⁴ The frequent citation of my article probably reflects its role in calling attention to the potential of this field."

1. Parshall G W. Homogeneous catalytic activation of C—H bonds. *Account. Chem. Res.* 8:113-17, 1975.
2. The homogeneous catalytic activation of C—H bonds. *Catalysis* 1:335-68, 1977.
3. Parshall G W, Thors D L & Tulip T H. Activate C—H bonds. *ChemTech* 12:571-6, 1982.
4. Dehaud J & Pfeiffer M. Cyclometallated compounds. *Coord. Chem. Rev.* 18:327-52, 1976.