

This Week's Citation Classic®

Appleton T G, Clark H C & Manzer L E. The *trans*-influence: its measurement and significance. *Coord. Chem. Rev.* 10:335-422, 1973.

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This paper reviewed the evidence from a variety of techniques for the existence of a *trans* influence (the tendency of a ligand in a metal complex to weaken the bond *trans* to itself) and compared results from different techniques. [The *SCI*® indicates that this paper has been cited in over 580 publications.]

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Russian chemists in the 1920s and 1930s¹ noted that in square planar platinum(II) compounds, some ligands have a tendency to promote substitution reactions at the coordination site *trans* (or opposite) to themselves, and they defined this kinetic effect as the *trans* effect. Up to the early 1960s, there was considerable argument about whether this effect was due in part to weakening of the *trans* bond in the ground state of the complex or whether it could be discussed only in terms of the transition state of the substitution reaction. Up to that time, X-ray crystallography could not easily measure bond lengths accurately. Low-frequency vibrational spectroscopy was difficult, and there were few measurements of nuclear magnetic resonance (NMR) coupling constants between metal nuclei (for example, ¹⁹⁵Pt) and ligand nuclei. This situation changed quite rapidly as these techniques became routinely available. In a key paper in 1966, A. Pidcock *et al.*² coined the term

"*trans* influence," for the ground state bond weakening effect, and over the following years experimental results accumulated.

After completing my PhD at the University of Queensland in 1970, I began work as a postdoctoral fellow in Howard C. Clark's group at the University of Western Ontario. Malcolm Chisholm, Hideo Kurosawa (also postdoctoral fellows), Leo E. Manzer (then a graduate student), and I were working on aspects of the organometallic chemistry of platinum. We used NMR coupling constants routinely as a measure of *trans* influence, both to characterize new compounds and to provide information about the kinds of bonds that new ligands, such as alkoxy-carbenes, formed with platinum. In June 1971 we participated in a small inorganic chemistry conference, known as an "Inorganic Weekend," in Toronto, and presented three consecutive papers on our platinum work. Barry Lever, the editor of *Coordination Chemistry Reviews* was there, and after the meeting he wrote to Clark, suggesting that a review be written in this general area. After discussion, we decided that Leo and I should write a review on the *trans* influence. Leo and I gathered the references together, and I wrote most of the text, which Clark then reviewed. It turned out to be a very long review, which was almost ready for submission when I left the group in August 1972.

I think the review was successful because sufficient data could be presented at that time to convince most readers that the *trans* influence really did exist, for platinum and other metals, and because of the detailed lists of *trans*-influence orders and spectroscopic data that allowed workers to put their own data into a wider context simply by citing it.

Much of my research work since then has involved *trans*-influence measurements, usually as a routine tool, but sometimes providing the empirical basis for further applications, for example, with ³¹P NMR,³ and, more recently, ¹⁵N NMR.⁴

1. Grinberg A A. The nature of "trans effect." *Acta Physicochim. URSS* 5:373-82, 1935. (Cited 20 times since 1955.)
2. Pidcock A, Richards R E & Venanzi L M. ¹⁹⁵Pt-³¹P nuclear spin coupling constants and the nature of the *trans*-effect in platinum complexes. *J. Chem. Soc. A* 1966:1707-10. (Cited 290 times.)
3. Appleton T G & Bennett M A. Preparation and properties of hydroxo(methyl)-1,2-bis(diphenylphosphino)ethaneplatinum(II). A *trans*-influence series including σ carbon donor ligands based on platinum-phosphorus coupling constants. *Inorg. Chem.* 17:738-47, 1978. (Cited 80 times.)
4. Appleton T G, Hall J R & Ralph S F. ¹⁹⁵Pt and ¹⁹⁵Pt NMR spectra of platinum ammine complexes: *trans*- and *cis*-influence series based on ¹⁹⁵Pt-¹⁵N coupling constants and ¹⁵N chemical shifts. *Inorg. Chem.* 24:4685-93, 1985. (Cited 5 times.)