Quantification of the trans influence in d^8 square planar and d^6 octahedral complexes: a database study

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Quantification of the trans influence in d^8 square planar and d^6 octahedral complexes: a database study

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A systematic search of the Cambridge structural database was undertaken to quantify the trans influence in square planar and octahedral transition metal compounds. For square planar geometry, d^8 metal centers were studied, while octahedral searches focused on low-spin d^6 complexes. Two probe ligands (PL) were used to measure the effect of the trans ligand (TL), chloride, and triphenylphosphine (PPh_3). For the TLs $O=CX_2$, NR_3, pyridine, and Cl^- (X = any non-metal, R = H or hydrocarbon), the effects on the metal–probe ligand (M–PL) distance were statistically equal and were taken as essentially no trans influence. The other ligands studied showed significant decrease in the mean M–PL bond order, relative to the above ligands: $SR_2 = 0.941$; $S=CX_2 = 0.887$; $PPh_3 = 0.825$; phenyl = 0.743; $CR_3 = 0.719$; hydride = 0.685. Some variation in the trans influence is observed, based on the geometry of the metal center and the PL. In general, electron-donating, σ-bonding ligands lead to a larger trans influence, but π-bonding effects can also be important, particularly when the probe ligand also has π-bonding properties.

Keywords: Trans effects; Octahedral transition metal complexes; Square planar transition metal complexes

1. Introduction

The trans effect has long been a topic of interest in transition metal chemistry and continues to have important applications. This effect was first studied by workers in the former Soviet Union: Chernyaev [1] established the idea that trans ligands (TLs) have a particularly strong effect on dissociation rates, and Grinberg [2] and Nekrasov [3] proposed a theoretical background for the observed effect, based on polarization. In 1962, Basolo and Pearson [4] defined the trans effect as *the labilization of ligands trans to certain other ligands*, and a general consensus developed that this effect has two components: a mechanistic effect (the kinetic trans effect) and a structural (or bond-lengthening) effect (the structural trans effect). In 1966, Pidcock *et al.* [5] coined the term *trans influence* for the structural trans effect. Mason *et al.* [6, 7] used crystallographic data from square planar Pd (II)–Cl compounds to establish a trans influence series: $SiR_3 > H > PR_3 > C=C > Cl > O$ (acac). Subsequent work, based on a variety of techniques, has led to some additions and reshufflings of Mason's proposed series; reviews of this work for both square planar and octahedral geometries are available [8–13]. Despite its long history, the trans effect continues to be a subject of interest, particularly due to the increasing role of transition

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metal centers in synthetic organic chemistry [14–17]. Additionally, the chemistry of many inorganic molecules of biological interest, including cobaloximes and other heme-related species, may be understood in the context of the trans effect [18–22].

Although there has been much work done on the overall trans effect and the trans influence, it has often proved difficult to produce a systematic set of data, hence the proliferation of different series concerning the magnitude of the effect for various TLs. There are many practical reasons why this should be the case, but the growth of the Cambridge Structural Database (CSD) [23] provides the possibility of producing a more systematic data-set, since the large number of available structures could yield a wide range of metal–TL combinations. The review of Coe and Glenwright [13] included an impressive amount of crystallographic data for octahedral compounds, but it was neither systematic nor exhaustive, and a very large number of compounds have entered the database since the publication of that review. Additionally, the improvements in computational methods have allowed researchers to successfully apply these techniques to transition metal compounds [15, 24–28]. However, due to the lack of systematic structural data, it is not entirely clear how well these computations reproduce an effect as subtle as the trans influence, and what difference increasing levels of theory may make in obtaining accurate results. For the above reasons, a systematic study of the CSD was undertaken, focusing on the structural consequences of the trans influence in both square planar and octahedral species.

2. Experimental

2.1. *Database search*

Searches were initially carried out on the 2011 release of the CSD [23] and were checked using the 2012 release. The search procedure was similar to previous work from this lab [29]. Specifically, searches were made under the following conditions, using the generic square planar and octahedral structures shown in figure 1:

- Metals (M) were for square planar: Au(III), Ni(II), Pd(II), Pt(II), and Rh(I) – all d^8 metal centers. For octahedral: Pt(IV), Co(III), Rh(III), Ir(III), and Ru(II) – all d^6
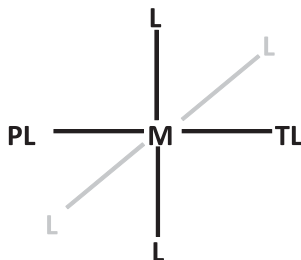
- PL = probe ligand
- TL = trans ligand
- L (two for square planar, four for octahedral)

Figure 1.   Generic CSD search structure.

metal centers (only low-spin complexes were used, suspected high-spin Co(III) complexes were omitted). The possibility of including other metal centers in this study was pursued, but they did not produce sufficient CSD hits to merit inclusion. No other metal atoms were allowed in the covalently bound species of interest.

- Probe ligands (PL) were terminal chloride and unsubstituted triphenylphosphine (PPh$_3$). These were chosen because both ligands are very common across a wide range of transition metal compounds, and both ligands often serve as leaving groups in proposed reaction mechanisms.
- TL types were: O=CX$_2$, pyridine, NR$_3$, Cl$^-$, SR$_2$, S=CX$_2$, PPh$_3$, η^2-R$_2$C=CR$_2$, CO, C$_6$F$_5$$^-$, phenyl$^-$, CR$_3$$^-$, and H$^-$ (where X is any moiety containing only nonmetal atoms and R is H or a hydrocarbon moiety). The exact CSD search fragments are available as Supplemental materials. Cl$^-$, CO, C$_6$F$_5$$^-$, and H$^-$ define specific ligands, but the other types leave room for many substituent groups. These were allowed as long as the TL was not part of a tridentate (or higher) ligand. Also, highly fluorinated ligands (other than C$_6$F$_5$) were omitted from the collected data-sets.
- The required PL–M–TL angle was in the range of 168°–180°.
- The cis ligands (L) could be any compound, but the binding atoms were limited to B, C, N, O, Si, P, S, C, Br, or I. No tetradentate ligands, such as porphyrins, were allowed.
- CSD searches specified R < 10%, with no disordered or polymeric structures.
- Outliers were deleted from the final data-set.

The results of these CSD searches are shown in tables 1 and 2, for square planar and octahedral compounds, respectively. The various combinations of metal center, PL, TL, and geometry resulted in 122 separate data-sets, with the number of observations (N_{obs}) ranging from 3 to 642 crystallographic structures.

3. Results and discussion

3.1. *Validity of the collected data*

In general, CSD studies are unavoidably noisy, as there are a variety of factors that could potentially add error to the compiled data. The protocol outlined above works to minimize some of these factors, but quantified measures of data validity are an important check for this type of study. One way to assess the validity of quantifying the trans influence through database methods is to look at the standard deviations of the entries in tables 1 and 2. Of the 122 data-sets in these tables, these standard deviations can be categorized as follows: $\sigma \leqslant 0.010 = 31$ (25%); $0.010 < \sigma > 0.020 = 71$ (58%); $\sigma \geqslant 0.020 = 20$ (16%). When one considers that the typical crystallographic esd's on the metal–probe ligand (M–PL) distances (M–Cl or M–P) are in the 0.005 Å range, and that there are a wide variety of cis ligands included in this compiled data, these standard deviations indicate a reasonably tight grouping of the compiled data.

While the cis ligands are generally expected to influence metal–ligand distances less than TLs, it is possible that variation in the cis ligands could bias the compiled data. This possibility was addressed by examining the data-sets in tables 1 and 2 with large N_{obs}. These data-sets were scanned for common cis ligands to form subsets with specified cis

Table 1. M–PL distances – square planar metal centers.

	Au(III)	Ni(II)	Pd(II)	Pt(II)	Rh(I)
PL = Cl					
$X_2C=O$	2.265(12) *4*		2.290(9) *22*	2.287(11) *31*	
Pyridine	2.263(12) *55*	2.162(4) *4*	2.290(14) *358*	2.296(10) *219*	
NR_3	2.276(8) *11*		2.304(17) *177*	2.309(12) *201*	
Cl	2.277(14) *217*	2.171(14) *30*	2.303(18) *642*	2.300(12) *485*	
Mean, CCL	**2.270**		**2.297**	**2.298**	
SR_2	2.287(6) *3*		2.317(13) *121*	2.315(10) *88*	
$X_2C=S$	2.322(16) *18*	2.189(11) *11*	2.335(17) *32*	2.330(10) *19*	
PPh_3			2.369(17) *106*	2.356(15) *67*	2.391(15) *16*
CO				2.296(11) *11*	2.360(18) *136*
$\eta^2-C=C$			2.320(10) *12*	2.321(14) *58*	2.358(10) *10*
C_6F_5	2.321(12) *3*		2.382(7) *3*	2.367(9) *4*	
Phenyl	2.369(13) *41*	2.242(16) *11*	2.405(21) *241*	2.406(13) *72*	
CR_3	2.379(11) *4*		2.415(31) *30*	2.419(12) *9*	
H				2.405(11) *3*	
PL = PPh₃					
$X_2C=O$			2.243(24) *16*	2.239(15) *34*	2.233(15) *8*
Pyridine	2.304(15) *5*	2.187(5) *3*	2.251(16) *22*	2.236(15) *15*	2.245(23) *3*
NR_3			2.250(9) *42*	2.235(19) *14*	2.258(8) *6*
Cl			2.253(9) *26*	2.248(14) *23*	
Mean, CCL			**2.249**	**2.239**	**2.245**
SR_2				2.279(23) *4*	
$X_2C=S$		2.202(14) *36*	2.311(19) *14*	2.291(13) *70*	2.274(7) *5*
PPh_3		2.232(17) *21*	2.334(11) *176*	2.311(16) *172*	2.328(15) *26*
$\eta^2-C=C$					2.333(12) *7*
C_6F_5				2.283(4) *3*	
Phenyl				2.308(13) *11*	
CR_3	2.387(7) *7*			2.309(15) *16*	

Distances in Å with standard deviation in parentheses. Number of observations in *italics*. (CCL is "classic coordination ligands.")

ligands that can be compared against the mean M–PL distance of the entire data-set to establish validity. Table 3 contains the results of this procedure: 26 subsets were analyzed, 16 with square planar geometry and 10 with octahedral geometry. None of these cis ligand specified subsets show a mean more than 1 σ different than the mean for the analogous data-set. In only two of the 26 subsets is the mean >0.010 Å different than the mean for the analogous data-set, and the average difference between subset and data-set means is 0.004 Å, which is very similar to the crystallographic esd's for these distances. Therefore, particularly in data-sets with large N_{obs}, it is unlikely that variation in cis ligands has any significant effect on the compiled mean M–PL distances. However, in data-sets with small N_{obs}, it is possible that cis ligands, as well as effects such as substituent groups, steric effects, and crystal packing, could bias the mean M–PL distance, so the values with small N_{obs} should be carefully considered.

3.2. *M–PL distances*

The data in tables 1 and 2 show the effect of the TLs on the M–PL distance, with the PL being either Cl or PPh_3. When discussing M–PL distances, a longer distance indicates a stronger trans influence induced by the TL. The trends in the mean M–PL distances show a consistent pattern across all metal centers and both geometries and PL. In each case,

Table 2. M–PL distances – octahedral metal centers.

	Pt(IV)	Co(III)	Rh(III)	Ir(III)	Ru(II)
PL = Cl					
X$_2$C=O	2.297(16) *21*		2.333(12) *11*	2.350(13) *6*	2.380(24) *29*
Pyridine	2.304(6) *40*	2.242(15) *32*	2.334(11) *28*	2.356(15) *22*	2.404(21) *42*
NR$_3$	2.315(10) *114*	2.258(13) *59*		2.380(11) *9*	2.365(10) *4*
Cl	2.316(13) *325*		2.341(14) *172*	2.350(19) *86*	2.396(19) *143*
Mean, CCL	**2.308**		**2.336**	**2.354**	**2.313**
SR$_2$	2.331(11) *4*		2.355(6) *6*		
X$_2$C=S	2.356(12) *5*		2.397(5) *6*	2.441(4) *3*	2.386(10) *6*
PPh$_3$			2.393(19) *6*	2.411(10) *5*	2.464(15) *32*
CO			2.371(10) *10*	2.383(16) *22*	2.421(19) *173*
Phenyl	2.427(19) *11*	2.378(31) *4*	2.490(5) *5*	2.474(19) *22*	2.494(22) *5*
CR$_3$	2.449(28) *13*		2.504(35) *4*	2.489(21) *6*	
H			2.502(10) *6*	2.502(17) *35*	2.537(27) *26*
PL = PPh$_3$					
X$_2$C=O					2.303(9) *8*
Pyridine					2.337(23) *14*
NR$_3$			2.312(32) *3*		2.311(18) *6*
Cl			2.295(27) *3*	2.320(17) *3*	2.302(17) *30*
Mean, CCL					**2.313**
X$_2$C=S					2.347(21) *8*
PPh$_3$			2.380(14) *49*	2.378(20) *92*	2.395(20) *397*
Phenyl				2.432(8) *6*	
CR$_3$		2.403(16) *10*	2.471(15) *5*		
H					2.442(34) *3*

Table 3. Subsets with specified cis ligands.

Square planar				Octahedral			
Specified cis ligand (L) subset	Mean(σ) N_{obs}		Difference from data-set mean (Å)	Specified cis ligand (L) subset	Mean(σ) N_{obs}		Difference from data-set mean (Å)
Trans-Pd(Cl)$_2$(L)$_2$ data-set mean = 2.303				*Trans-Ru(Cl)$_2$(L)$_4$ data-set mean = 2.396*			
2 NR$_3$	2.303(9) *54*		0	4 pyridine	2.403(16) *7*		0.007
2 pyridine	2.303(10) *68*		0	2 pyridine, 2 CO	2.391(7) *11*		0.005
2 Cl$^-$	2.306(9) *88*		0.003	*Trans-Rh(Cl)$_2$(L)$_4$ data-set mean = 2.341*			
2 S=CX$_2$	2.309(7) *7*		0.006	4 Cl$^-$	2.344(2) *6*		0.003
2 PPh$_3$	2.300(11) *46*		0.003	Cl$^-$, 3 pyridine	2.341(7) *8*		0
Trans-Pt(Cl)$_2$(L)$_2$ data-set mean = 2.300				*Trans-Pt(Cl)$_2$(L)$_4$ data-set mean = 2.316*			
2 NR$_3$	2.297(6) *17*		0.003	4 Cl$^-$	2.319(10) *80*		0.003
2 pyridine	2.302(7) *17*		0.002	2 Cl$^-$, 2 NR$_3$	2.316(8) *13*		0
2 Cl$^-$	2.303(11) *74*		0.002	2 Cl$^-$, 2 py	2.316(7) *14*		0
2 PPh$_3$	2.309(7) *14*		0.009	2 Cl$^-$, 2 O=CX$_2$	2.312(5) *5*		0.004
Trans-Pd(PPh$_3$)$_2$(L)$_2$ data-set mean = 2.334				*Trans-Pd(PPh$_3$)$_2$(L)$_4$ data-set mean = 2.395*			
2 Cl$^-$	2.336(11) *12*		0.002	2 Cl$^-$, 2 pyridine	2.386(15) *6*		0.009
2 S=CX$_2$	2.346(15) *7*		0.012	2 Cl$^-$, 2 O=CX$_2$	2.409(10) *9*		0.014
Cl$^-$, CR$_3$	2.330(9) *10*		0.004				
Cl$^-$, phenyl	2.329(9) *27*		0.005				
Trans-Pt(PPh$_3$)$_2$(L)$_2$ data-set mean = 2.311							
2 C≡CR$^-$	2.308(13) *19*		0.003				
2 S=CX$_2$	2.317(4) *5*		0.006				
Cl$^-$, phenyl	2.309(11) *8*		0.002				

when the TL is O=CX$_2$, pyridine, NR$_3$ or Cl, the M–PL distance stays nearly constant. This group of four ligands (O=CX$_2$, pyridine, NR$_3$, and Cl) will be referred to as the "classic coordination ligands," and the calculated mean for these ligands is given in tables 1 and 2. For the square planar metal centers, there is very little variation between these four ligands, with the NR$_3$ and Cl TLs inducing slightly longer M–PL distances than O=CX$_2$ or pyridine. The octahedral metal centers show slightly more M–PL variation induced by these TLs, particularly due to the surprisingly strong effect of pyridine with octahedral Ru(II).

For the sulfur- and phosphorus-binding ligands, the trans influence increases in the order of SR$_2 <$ S=CX$_2 <$ PPh$_3$. One way to assess the trans influence due to these ligands is to look at the increase in the M–PL distance, compared to the mean of the classic coordination ligands. The mean increases from the M–PL distances for the classic coordination ligands are: SR$_2 = 0.023$ Å; S=CX$_2 = 0.045$ Å; PPh$_3 = 0.072$ Å. For most metal centers, the increase in M–PL distance induced by S=CX$_2$ and PPh$_3$ is large (>2σ) compared to the mean of the classic coordination ligands, and the fact that the trend holds well across the various metal–probe combinations additionally increases the validity of these results. For the carbon-binding ligands, η^2-C=C and CO display a modest trans influence, with trans η^2-C=C inducing an increase of 0.023 Å in square planar M–PL distances, and trans CO lengthening octahedral M–PL distances by 0.033 Å (in the case of trans CO bound to square planar Pt(II), no trans influence was observed). However, the ligands C$_6$F$_5$, phenyl, CR$_3$, and H show a very substantial trans influence. C$_6$F$_5$ has an effect similar in magnitude to that of PPh$_3$, lengthening M–PL by 0.062 Å. Phenyl, CR$_3$, and hydride have the largest trans influence of any ligands investigated, with their average increase in M–PL distance being 0.113, 0.123, and 0.141 Å, respectively, compared to the classic coordination ligands. This represents a very substantial weakening of the M–PL bond and should lead to significantly higher rates of dissociation.

3.3. *Relative bond orders*

An alternate, and perhaps more intuitive, way to understand the changes in the M–PL bond is in the context of relative bond orders. The M–PL distances can be converted to bond orders using the equation first suggested by Pauling [30] and later refined by Brown [31], O'Keefe and Breese [32]:

$$bo = \exp((r_{ij} - d_{ij})/c) \tag{1}$$

where d_{ij} is the observed distance between atoms i and j, r_{ij} is the "single bond expectation" distance between the same two atoms, and c is a constant established by curve-fitting (for bonds containing transition metal atoms, c is usually assumed to be 0.37 [31]). This equation can be very useful, but a limitation of it is that it is highly dependent on the value of r_{ij}. Since, in this work, the purpose of these calculations is comparative, the r_{ij} value for any combination of metal and PL will be taken as the mean M–PL distance when a classic coordination ligand is in the trans position ($d_{ccl\ mean}$), as listed in tables 1 and 2. Therefore, the above equation becomes:

$$rbo = \exp((d_{ccl\ mean} - d_{m-pl})/0.37) \tag{2}$$

and what is calculated (rbo) is the bond order *relative* to the M–PL bond when a classic coordination ligand (O=CX$_2$, pyridine, NR$_3$, or Cl) is in the trans position. The results of these calculations are given in table 4 for all 11 M–PL combinations having data-sets for at least three of the four classic coordination ligands. Unlike the raw bond distances, a stronger trans influence is indicated by a *lower* rbo value. The strength of using relative bond orders is that a variety of metal centers and ligands can be compared on a consistent, quantified scale. Historically, structural studies of the trans influence have focused on a series of similar compounds with the same PL and metal center [6, 7, 33, 34]. By using the relative bond order, it is possible to compare different metal centers, PL, and coordination geometries.

The trends identified in the M–PL distances are also in evidence in the rbo values, and these trends are displayed in chart form in figure 2. The values near rbo = 1.0 are clear for the classic coordination ligands, and the increasing trans influence of SR$_2$, S=CX$_2$, and PPh$_3$ are also clearly displayed, with overall mean rbo values of 0.941, 0.887, and 0.825, respectively. The very strong trans influence of the sigma-bonding Ph$^-$, CR$_3$$^-$, and H$^-$ ligands is also very evident. Additionally, table 4 and figure 2 appear to show some small but interesting differences in the rbo values, based on geometry and PL. For instance, in the square planar complexes with CR$_3$ as the TL and chloride as the PL, the three rbo values are very closely grouped, averaging 0.731. When the geometry is changed to octahedral, with the same trans and PL, the rbo values are again closely grouped, but about a much lower mean of 0.670. This increase in sensitivity to the TL in octahedral complexes, relative to square planar, is also observed for the phenyl and hydride ligands. Finally, the collected data also indicates that the PPh$_3$ PL is less influenced by the alkyl-bound organic ligands and hydride than Cl. There are four instances where the same metal center and TL (sq. planar Pd(II)–C$_6$F$_5$, Pd(II)–phenyl, Pd(II)–CR$_3$, and octahedral Ru(II)–hydride) have data-sets for both the chloride and PPh$_3$ PL, and in each case, the M–PL rbo is lower (greater trans influence) for chloride than for PPh$_3$, with the difference between the rbo values for the two PL averaging 0.072. The sulfur-binding ligands and PPh$_3$ also appear to show some differences based on PL, though they are smaller in magnitude.

3.4. *Discussion*

The trans influence is considered to be strongest with strong σ-binding ligands, and indeed, the alkyl-binding organic ligands and hydride have the greatest effect. It is difficult to quantify the σ-donating strength of ligands, however, the results of this study do not appear to completely match the generally accepted series. A popular inorganic textbook [35] gives the following series for σ-donating strength of ligands:

$$OH^- < NH_3 < Cl^- < Br^- < CN^-, CH_3^- < I^- < SCN^- < PR_3, \ H^-$$

While the lower end of the series (those ligands with little or no trans influence) does look similar to the results of this study, some of the ligands at the higher end appear to be out of place. Looking simply at the mean rbo values, the following trend is observed:
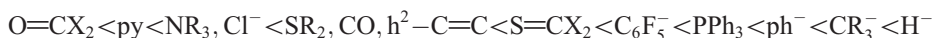
$$O{=}CX_2 < py < NR_3, Cl^- < SR_2, CO, h^2{-}C{=}C < S{=}CX_2 < C_6F_5^- < PPh_3 < ph^- < CR_3^- < H^-$$

Table 4. Relative bond orders (rbo, from equation (2)) of the M–PL bond, by TL.

Geometry: Square planar

PL / Metal center	Cl — Au(III)	Pd(II)	Pt(II)	Mean	PPh$_3$ — Pd(II)	Pt(II)	Rh(I)	Mean	Square planar mean
$X_2C{=}O$	1.014	1.018	1.030	1.021	1.017	1.003	1.034	1.018	1.020
Pyridine	1.020	1.018	1.005	1.014	0.995	1.009	1.001	1.002	1.008
NR_3	0.985	0.981	0.971	0.979	0.998	1.012	0.966	0.992	0.985
Cl	0.982	0.983	0.995	0.987	0.990	0.977		0.984	0.985
SR_2	0.956	0.947	0.955	0.953		0.898			0.939
$X_2C{=}S$	0.869	0.902	0.917	0.896	0.846	0.869	0.925	0.880	0.888
PPh_3		0.823	0.855	0.837	0.795	0.824	0.800	0.806	0.819
CO			1.005	1.005					–
η^2–C=C		0.939	0.940	0.940					0.940
C_6F_5	0.872	0.794	0.830	0.832		0.888			0.846
Phenyl	0.766	0.746	0.747	0.753		0.830			0.772
CR_3	0.745	0.726	0.721	0.731		0.828			0.75
H			0.749	0.749					

Geometry: Octahedral

| PL / Metal center	Cl — Pt(IV)	Rh(III)	Ir(III)	Ru(II)	mean	PPh$_3$ — Ru(II)	Octahedral mean	Overall mean
$X_2C{=}O$	1.032	1.008	1.010	1.017	1.017	1.028	1.019	1.019
Pyridine	1.010	1.005	1.054	0.953	1.006	0.938	0.992	1.001
NR_3	0.981	0.987	0.931	1.059	0.990	1.006	0.994	0.993
Cl	0.978		1.010	0.974	0.987	1.031	0.996	0.991
SR_2	0.939	0.950			0.945		0.945	0.941
$X_2C{=}S$	0.878	0.848	0.789	1.001	0.879	0.913	0.886	0.887
PPh_3		0.857	0.856	0.810	0.841	0.802	0.831	0.825
CO		0.910	0.923	0.910	0.914		0.914	0.937
Phenyl	0.724	0.660	0.722	0.747	0.713		0.713	0.743
CR_3	0.683	0.635	0.693		0.670		0.670	0.719
H		0.638	0.669	0.665	0.658	0.706	0.670	0.685
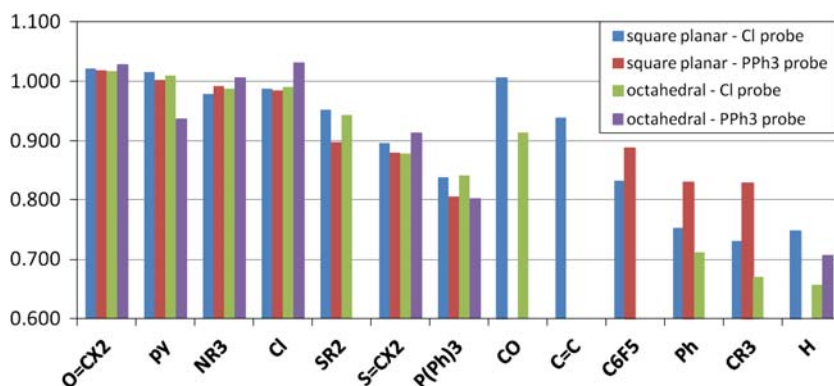
Figure 2. Trends in M–PL relative bond order (*y*-axis) based on variation of the TL.

However, a close inspection of table 4 and figure 2 shows the situation to be more complex. As noted above, there appears to be a least three trends, in addition to the overall trend in mean rbo values, that may be meaningful:

- For the SR_2, $S=CX_2$, and PPh_3 TLs, the trans influence is generally larger for the PPH_3 PL than for chloride PL.
- For the $C_6F_5^-$, $C_6H_5^-$, CR_3^-, and H^- TLs, the reverse is true – the trans influence is much larger for the chloride TL than for PPH_3.
- For the CO, $C_6H_5^-$, CR_3^-, and H^- TLs, octahedral geometry shows a larger trans influence than square planar geometry.

Perhaps, the best way to rationalize the trans influence is as a competition for bonding to the metal center between ligands with co-linear metal–ligand bond axes. Grinberg [2] and Nekrasov [3] first proposed the polarization model to explain the trans influence, and many of the above trends can be understood in the context of this idea. In essence, their model asserts that electron-donating TLs induce a charge buildup on the metal center that is primarily focused in the bond axis, therefore, weakening the bond to the PL. Put in more modern terms, one may conceive of this as either a competition for favorable charge distribution (electrostatic bonding) or σ-bonding orbitals (covalent bonding), or a combination of both. Concerning the general trend in overall rbo values, the above model yields a satisfying result. In the case of the anionic TLs, the polarizing/σ-donation effect can be quantified through the Hammett field (F) parameter [36], which decreases with increasing electron donation. Figure 3 plots this parameter against the mean rbo value (with PL = Cl^-) for the anionic ligands. The result is a smooth (though nonlinear) function which shows a stronger trans influence for more electron-donating species, such as CR_3^- and H^-. No Hammett parameters exist for the neutral ligands, so they cannot be included in figure 3, but it should be noted that the ligands binding through the most electronegative atoms ($O=CX_2$, py, NR_3) have the smallest trans influence, and those binding through less electronegative atoms (SR_2, $S=CX_2$, PPh_3) have an increasingly large effect. Based on these results, it appears that the polarization/σ-donation effect of the TL is the primary factor in weakening the M–L bond to the PL.

The increased sensitivity to TLs in the octahedral geometry (which is also well illustrated in figure 2) may also be rationalized in the context of the polarization model. In
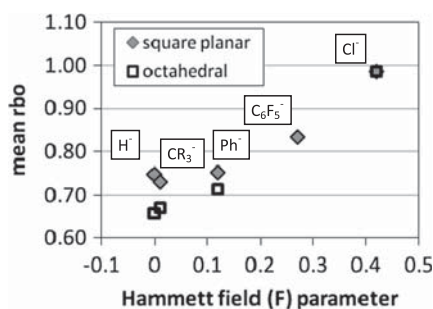
Figure 3.   Plot of Hammett field (F) parameter vs. mean relative bond order (PL = Cl) for the anionic ligands Cl, C_6F_5, phenyl, CR_3, and hydride.

square planar geometry, the *z*-axis is unused, and some of the charge build-up induced by the TL may "leak out" above and below the coordination plane, slightly reducing the bond weakening effect on the PL. In octahedral geometry, there is no place for the excess charge to go, so the PL feels the full polarization effect.

Finally, concerning the differential effect of these TLs on the two different PL, it appears that at least two different effects must be significant, since the trends change from the organic ligands (and hydride) to the sulfur- and phosphorus-binding ligands. Again, this can be understood in terms of a competition between ligands. In the organic ligands and hydride, σ-bonding and polarization are the overwhelming concern, as they are for chloride. However, coordination to a metal center by the PPh_3 ligand is considered to have a significant π-bonding component [13, 37, 38]. Therefore, the stronger σ-donating ligands can be expected to have a stronger effect on the trans M–Cl bond than on the trans M–PPh_3 bond, since for the M–Cl bond, the trans and PL are both competing for the same type of bonding. However, in the sulfur-binding ligands and PPh_3, where π-bonding effects are also important, the π-bonding TLs compete for this bonding mode to the metal, and therefore weaken the M–PPh_3 bond more so than the M–Cl bond, where π-bonding is unimportant. This can particularly be seen when the PPh_3 TL is compared to Ph^- and CR_3^-. When PPh_3 is also the PL, the PPh_3 TL has a larger effect than either of the organic (σ-donating) ligands. However, when Cl^- is the PL, the organic ligands have a much larger effect than does PPh_3. Clearly, polarization is still the primary factor in the trans influence of these sulfur- and phosphorus-binding ligands, but π-bonding properties must also be taken into account when π-bonding is also important in the PL.

4. Conclusion

Systematically compiled data from the CSD give a quantification of the trans influence for the ligands O=CX_2, NR_3, pyridine, Cl^-, S=CX_2, SR_2, PPh_3, CO, η^2–C=C, $C_6F_5^-$, Ph^-, CR_3^-, and H^-, at least as they effect the metal–ligand bond to the PL Cl^- and PPh_3 in square-planar d^8 and octahedral d^6 (low-spin) complexes. These results show that O=CX_2, NR_3, pyridine, and Cl^- have little or no trans influence, S=CX_2, SR_2, CO, and η^2–C=C show a modest trans influence, and PPh_3, $C_6F_5^-$, Ph^-, CR_3^-, and H^- display the largest effect in lengthening the trans M–L bond. In quantified terms, the ligands found to have the largest effect, such as CR_3^- and H^-, resulted in a lengthening of the trans M–L bond by >0.1 Å, and a reduction of the bond order by ~30%, relative to the ligands with no trans influence. The polarizing/σ-bonding ability of the ligands appears to be the greatest

factor in the observed trans influence, with electron-donating species having the larger effect. However, the π-bonding character of the ligand is also a factor in the trans influence, particularly if both the trans and PL engage in significant π-bonding to the metal center.

Acknowledgments

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