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Review

Predicting the net donating ability of phosphines—do we need sophisticated theoretical methods?

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Dedicated to Prof. Michael I. Bruce on the occasion of his 65th birthday, with my warmest congratulations and very best wishes.

Contents

Abstract

Several approaches to quantify and classify the electronic properties of phosphines and similar ligands experimentally are reviewed and compared to recent attempts to calculate these properties with theoretical methods.

Keywords: Tolman electronic parameter; Theoretical calculations; Molecular electrostatic potential; QALE

1. Introduction

In order to investigate the electronic properties of ligands one needs to find a probe that responds effectively and sensitively to changes in the electronic properties of said ligands. Two such probes became the focus of attention, transition metal nitrosyl [1–3] and carbonyl [3–18] complexes. Their IR spectra display very specific bands for the nitrosyl and carbonyl groups. The resonances in the IR spectra for these groups are very sensitive towards alterations in tertiary phosphines [18] and other ligands. As NO^+ is isoelectronic and for the present purpose isostructural to CO, it is sufficient to explain this phenomenon for carbonyl. The arguments for the nitrosyl ligand are similar.

The position of the νCO bands in the IR-spectrum of a transition metal depend on the electronic situation at the metal. The CO ligand acts with its electron lone pair as a σ-donor

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towards the metal. The metal in turn can transfer electron density into the 5s (s^*_σ) antibonding orbital of the CO ligand, weakening the CO bond and shifting the νCO band towards lower wavenumbers [19]. If a CO ligand is replaced by a tertiary phosphine then the phosphine itself will act as a σ-donor with its electron lone pair towards the metal. This renders the metal more electron rich. This increased electron density on the metal can then be transferred towards the CO groups and the phosphine ligands. The extend of this backbonding is dependent on the π-acceptor strength of the various ligands. As only the phosphine is altered and the other ligands (CO, Cp etc.) remain constant, the system can be used to measure the electronic properties of a series of phosphine ligands. Good π-acceptor properties are indicated by a shift of the νCO frequency towards higher wavenumbers [18]. However, as the shift of νCO frequency is only an indication for the net electron donating ability of the ligand, this is not sufficient proof for good π-acceptor strength.

As this holds true for any transition metal carbonyl complex (or nitrosyl complex for that matter), Tolman's famous statement "we could have chosen some other carbonyl complex, but $[Ni(CO)_3L]$ forms rapidly . . . even if L is very large" (L: tertiary phosphine) becomes understandable [18]. Indeed, before [6–17] and after [20–22] Tolman other transition metal carbonyl complexes were chosen for various reasons and recently considerable effort was invested to calculate the respective νCO frequencies with a range of theoretical methods [23–28].

The main objectives of the present article are to give an overview of the existing scales for the experimental determination of the net donating ability of phosphines, why they have been developed and how they are interrelated as well as introducing the growing field of predicting the net donating ability of phosphines using theoretical methods. This article is intended as a guide for the synthetic chemist and for this reason the theoretical methods will not be discussed in detail. The efforts to predict the electronic properties and to reproduce existing experimental scales will be discussed in terms of their practical applicability.

2. The Strohmeier approach

In the 1960s, Strohmeier et al. investigated the σ-donor ability and π-acceptor strength of various ligand classes, amongst them nitriles [9,11], isonitriles [11,30], sulfoxides [6,10,29] and phosphines [7,31]. They were interested in establishing a "spectroscopic series" [2,7] for the ligand strength similar to the one familiar in classical coordination chemistry, a method to separate the σ-donor and the π-acceptor contribution of the M=L bond, and a classification of transition metal fragments according to their π-donor ability. For this reason, they carried out an elaborate research programme into the chemistry of transition metal carbonyl and nitrosyl complexes using a plethora of N, S, O and P-based ligand classes as standard donors.

Using arene chromium(0) tricarbonyl complexes in a photochemical ligand exchange reaction shown in Eq. (1):

$$[ArCr(CO_3)] + L \xrightarrow{h\nu} [ArCr(CO)_2L] + CO \quad (1)$$

they established that increasing the electron density on the arene ligand increases the electron density on the metal and thus favours backbonding towards the CO groups and the coordinated ligand [12,29]. This was monitored via the νCO stretching frequency. Increasing the electron density on the metal results in a smaller wavenumber for the corresponding νCO frequency.

In the same way Strohmeier et al. ordered the various metal carbonyl complexes ($[ArCr(CO)_2L]$, $[CpMn(CO)_2L]$, $[Fe(CO)_4L]$, $[M(CO)_5L]$ with M: Cr, Mo, W) according to their π-donor ability and arrived at the following series [10,30]: Mn ≫ Cr > W > Fe > Mo.

However, this order does not represent the transition metals correctly as part of the π-donicity comes from the aryl or Cp ligand. If one looks at the data [10,30] more carefully, then it becomes apparent that $[(C_6H_6)Cr(CO)_2]$ is a better π-donor than $[CpMn(CO)_2]$ meaning that a ligand corrected order of the above transition metals should read: Cr > W > Mo > Mn > Fe.

Having established the electronic influence of the central metal atom and the aryl substituent they turned their attention to the differences in the ligands themselves. They found a significant influence of the ligating atom (N, S, O, P) or more generally of the functional group the ligand uses to bond to the metal [6,7,9–12,29–31]. They summarised their findings in the well known series [12]: pyridine < nitrile ≪ PR_3 ∼ R_2SO ∼ isonitrile < CO.

At this point the fundamental principles necessary to quantify the electronic properties of a ligand were already well defined. These are:

- The ligand contribution consists of a σ-donor and a π-acceptor part (the π-acceptor part can be virtually 0).
- The ligand changes the electron density on the central metal.
- The electron density on the metal determines the degree of backbonding.
- The CO ligand acts as probe for the electron density on the central metal.

Two things were still missing, a better resolution to measure the influence of the rest R in the phosphine or the sulfoxide series and a way to quantify the results. The former Strohmeier et al. developed with the sulfoxide ligand family [29] and later adopted it to the phosphines [7], whereas the quantification was Tolman's great achievement [5,18].

As this article is mainly concerned with the electronic properties of phosphines rather than sulfoxides, it suffices to note that as the result of these experiments the sulfur-based ligands can be aligned in increasing π-acceptor strength in the series [29]: $R_2S < R_2SO < Ar_2SO < (RO)_2SO < SO_2$.

The σ-donor contribution was determined seperately using force constants and dipole moment determinations [12,32]. The same order of substituents was also found in the phosphine series. However, for the phosphines Strohmeier et al. defined classes numbered from I to VI in an attempt to quantify their results [7]. These classes were ordered in frequency bands and arranged according to increasing wavenumber. The classes I–III roughly correspond to the trialkyl phosphines (I), triaryl phosphines (II) and phosphites (III). These classes form the basis for Tolman's famous formula that quantifies the influence of the substituent on phosphorus in the $[Ni(CO)_3L]$ (L: tertiary phosphine) series.

3. The Tolman electronic parameter (TEP)

The first single equation relating all tertiary phosphines to a specific series of transition metal carbonyl complexes was the one describing the Tolman electronic parameter TEP [18] and is reproduced in Eq. (2):

$$\nu CO_{Ni} = 2056.1 + \Sigma\chi_j \quad (2)$$

where νCO_{Ni} refers to the A_1 band in the IR spectra of $[Ni(CO)_3L]$ (L: $PR^1R^2R^3$), 2056.1 is the A_1 band of $[Ni(CO)_3(PBu^t_3)]$ and χ_j is the effect the substituent R_j on phosphorus has on the frequency of the A_1 band of the respective $[Ni(CO)_3L]$ complex. $[Ni(CO)_3(PBu^t_3)]$ was chosen as the reference on the TEP scale where χ for $Bu^t = 0$ recognizing that PBu^t_3 is the most basic tertiary phosphine known to Tolman and thus the best σ-donor and worst π-acceptor.

Tolman's lasting achievement was his recognition of the fact that the σ-donor ability and the π-acceptor strength of tertiary phosphines are the two main components of the net donating ability of phosphines and can be jointly determined by measuring the A_1 band in the IR-spectrum of any respective transition metal carbonyl complex. Thus, the TEP describes the net donating ability of tertiary phosphines [18], although the property generally referred to in the context of TEP is the π-acceptor strength. However, since the differences in the σ-donor ability of tertiary phosphines are rather small, it is standard practice to interpret the νCO data in terms of the π-acceptor strength, a practice that can be misleading in certain cases.

It is worth remembering that an exact mathematical treatment would result in different equations for each of the classes or families defined by Strohmeier. But as Strohmeier has put it, the transition between the classes is gradual and the borderline cases can be treated as belonging to two classes simultaneously [7] The TEP, spanning the whole range of Strohmeier's classes, is an excellent approximation for all practical purposes, without being an exact match for any but the trialkyl phosphines.

The $[Ni(CO)_3L]$ scale of the TEP can be correlated with Strohmeier's $[CpMn(CO)_2L]$ system [31] using Eq. (3):

$$TEP = 0.711\,\nu CO_{Mn} + 692\,cm^{-1}, \qquad R = 0.970 \quad (3)$$

4. Alternative methods to determine the influence of substituents

As Tolman's IR-based method to determine the electronic influence of phosphine ligands on the νCO stretching frequency is based on alterations in the CO bond induced by the phosphine, it comes as no surprise that other research groups studied carbon 13 NMR chemical shifts [33–39] of these metal carbonyl complexes as well as C–P [40–43] and various M–P [44,45] coupling constants to determine the σ-donor and π-acceptor properties of phosphines. Early ^{13}C NMR studies were severely hampered by the low abundance and sensitivity of ^{13}C and as a consequence a sufficient database became available only after the advent of Fourier transform NMR in the mid 1970s.

The phenomena studied by ^{13}C NMR mirror those described by IR spectroscopy in the preceeding decade. Bodner first studied the influence of the substituents on the arene entity in $[ArM(CO)_3]$ (M: Cr, Mo, W) and found that the metal fragment acts as net electron donor on the carbonyl ligands [36,37]. The next logical step was the evaluation of the influence other ligands have on the chemical shifts of the carbonyl carbon atoms. Various metal carbonyl complexes including $[CpFe(CO)_2X]$ [46], $[CpMn(CO)_2L]$ [40,46], $[Ni(CO)_3L]$ [35,40], $[M(CO)_5L]$ (M: Cr, Mo, W] [33,34,38,40] and $[XRe(CO)_5]$ [47] (X: $1e^-$ donor ligand; L: $2e^-$ donor ligand) were investigated revealing a correlation between the k_2 stretching force constants and the *cis* carbonyl chemical shifts, whereas the same correlation to the respective *trans* carbonyls remained questionable [33]. The observed increase in the carbonyl stretching force constant is reflected by a shielding of the carbonyl resonance, which was attributed to a decrease in the magnitude of the separation between the ground state and the lowest lying electronic excited states with increasing transition metal → carbonyl π backdonation [35,48].

Besides the chemical shift values NMR spectroscopy knows a second vital parameter that can be used to monitor the immediate environment of a nucleus of interest, the coupling constants to neighbouring atoms. Thus, coupling constants have duly become the focus of attention. As the effect on coupling constants is greatest where the coupling constants have their highest absolute values, those compounds received preferential treatment where the phosphorus ligand is directly bound to another NMR active nucleus such as boron [49,50], tungsten [51], platinum [44] and selenium [44]. A qualitative relationship between $^1J_{PB}$ and the strength of the P–B dative bond was found [49,50]. The bond strength declines with the basicity of the phosphorus centre. Similar trends were found for the $^1J_{PSe}$ coupling constants with electron withdrawing thienyl and furyl substituents on phosphorus [44] as well as for the $^1J_{PPt}$ coupling constants [44].

The P–C coupling constants, studied to determine the influence of the substituents on the basicity of the phosphorus atom, show a complicated pattern of dependence. Not only is

it difficult to determine the sign (positive or negative) for the coupling constant, but the magnitude of the change in coupling constant upon complexation to a transition metal does not appear to correlate with the basicity of the phosphine [40].

NMR studies show a correlation (qualitatively and/or quantitatively) between the basicity of the phosphine ligand and the chemical shift value of the carbonyl carbon or the $^1J_{PE}$ coupling constant. However, in the absence of a thorough theoretical foundation [34], it cannot be expected that the observed correlations can be used to predict the exact basicity of unknown phosphines.

Other methods utilized to determine the basicity of phosphine ligands include the measurement of the pK_b value of the phosphine or rather the pK_a value of the corresponding phosphonium ion HPZ_3^+ [52,53] as well as the heat of protonation of M–PZ_3 complexes [54–63]. As the gas-phase proton affinity does not reflect the situation in solution, this easily to measure quantity is unsuitable for the determination of the phosphine basicity in the liquid phase [64]. The pK_a value of HPZ_3^+ is per definition generally an accurate measure of phosphine basicity as long as steric influences on the rate of protonation can be neglected. For very bulky phosphines there exists a significant deviation from the expected pK_a value that has to be taken into account [65,66]. Allman and Goel [52] have demonstrated that the pK_a values of PZ_3 if measured in $HClO_4$/nitromethane correlate excellently with Hammettt's σ_ι [67], Taft's σ^* [68], or Kabachnik's σ^ϕ [69] values depending on the substituents on phosphorus. However, some deviations were noted for phosphorus ligands of very low basicity and in particular phosphites. It needs to be remembered that pK_a measurements in non aqueous solutions can be very sensitive to choice of solvent and acid as was noted by Allman and Goel in this particular case [52]. The findings of Angelici for the heats of protonation of transition metal phosphine complexes are again similar [54]. On a series of metal complexes as diverse as *fac*-$[W(CO)_3(PZ_3)_3]$ [58,62], $[Cp^RM(PZ_3)_2X]$ (M: Os, Ru) [61], *cis*-$[M(CO)_2(L–L)_2]$ (M: Cr, Mo, W; L–L: bidentate phosphine) [60], [CpIr(CO)(PZ_3)] and $[Fe(CO)_3(PZ_3)_2]$ [56] he could demonstrate that the basicity of the metal complex closely follows that of the phosphorus ligand by determining the heats of reaction for the protonation of the metal complexes with dilute triflic acid CF_3SO_3H in dichloromethane or dichloroethane. Steric influences as measured by θ were only detected for sterically crowded complexes like *fac*-$[W(CO)_3(PZ_3)_3]$.

As we are concerned with a method to predict the net electron donating ability of ligands, we will follow the developments in the FTIR treatment of the problem since force constants and stretching frequencies can actually be calculated without taking recource to any experimental data. But before doing so we should first give consideration to a method that can resolve the net electron donating ability into its σ-donicity and π-acidity components.

5. Quantitative analysis of ligand effects (QALE)

Starting from the accepted belief that the net donating ability of phosphines (or any other similar ligand) is dependent on the σ-donor and π-acceptor properties of the ligand and influenced by steric factors, Giering et al. from the mid 1980s onwards tried to quantify these factors by means of a combination of regression and graphical analysis of the available experimental data [70]. These data include Tolman's electronic and steric parameters, χ and θ, respectively, as well as thermodynamic (ΔH^0, ΔS^0, and ΔG^0), kinetic (reaction rates), and electrochemical (ΔE^0) entities. The method known as quantitative analysis of ligand effects (QALE) relies on experimental data of known ligands and provides the resolution of the net donating ability of a ligand into the four QALE parameters χ_d, λ, E_{ar} and π_p (χ_d is the corrected TEP, λ denotes the steric switch based on Tolman's steric parameter θ, E_{ar} is the so called aromatic effect and π_p represents the π-acidity).

Originally, QALE was a comparatively simpler tool based on χ and θ alone [66,71–73], but over the years the original parameters were modified and new parameters discovered until presently a very sophisticated and detailed knowledge about the electronic and steric influences of phosphine ligands on metal centres is provided by QALE [27,74]. Tolman's steric parameter θ was included to describe a steric threshold to reflect the phenomenon that some reactions depend on the steric properties of the ligand once the steric bulk of the ligand exceeds a certain threshold value. A modification in the TEP was introduced twice by Giering et al, once to eliminate the π-acceptor contribution, χ_d denotes the pure donor ability without any π-acidity [75,76], and the second time to exclude the contribution from the "aromatic" effect E_{ar} [75], thus the term new χ_d. The E_{ar} is an additional electronic influence exerted by aromatic substituents on phosphorus and dependent on the number of such aryl groups [77,78]. As the E_{ar} is not limited to aryl rings, but appears to be a general property of non-alkyl substituents [79], the choice of name for the parameter is somewhat unfortunate and has its origin in the fact that it was first noticed and described for aryl substituents. The π_p parameter describes the π-acidic character of the ligand [80,81]. Hence, the two parameters of interest in the discussion of the relative influence of the σ-donor and π-acceptor contributions would be χ_d and π_p, the combination of which is TEP.

It has to be noted that QALE's foremost achievement is the separation of the TEP entity χ into the σ-donor and π-acceptor components χ_d and π_p, respectively [81]. It attains greater accuracy by incorporating steric effects (threshold value λ) and additional electronic factors (E_{ar}). As the steric threshold does not apply to the sterically unhindered Tolman complex $[Ni(CO)_3L]$ and the deviations caused by E_{ar} are usually small, a full QALE treatment is not required for routine estimates of χ.

For best results, the current version of QALE should be used as the method has been developed over the past two decades with substantial improvements in complexity and

performance. This can be seen by the QALE treatment of selected phosphine ligands. PCl_3 was first described as a pure σ-donor without any π-acidity on the basis of just two of the now four QALE parameters [82]. After the introduction of E_{ar} and utilization of a much broader database the verdict was altered to moderate π-acceptor. Similarly $P(CH_2CH_2CN)_3$ was always considered as a good π-acceptor on the basis of a high χ value. In a recent reevaluation, Giering and coworkers concluded that the ligand is indeed a poor π-acceptor and owes its high χ value to its even poorer σ-donicity [79]. This shows that a conclusion concerning the π-acidity of a ligand cannot be based on its χ value alone, even if the result were true in most cases.

The section would not be complete without mention of a competing system introduced by Drago [83–86] and sometimes referred to as ECW system. The system derives its name from the three contributing factors, the parameters $E_{a/b}$ and $C_{a/b}$ and the constant W. As Giering et al. have recently shown, ECW works well in cases where only χ and θ contributes and fails where a full set of four parameters would be required [87,88], a state of development in the ECW system that corresponds to QALE as it stood less than a decade ago.

We can conclude that QALE is arguably the best method to determine the stereoelectronic properties of a ligand in great detail and separate the individual effects. The drawback is QALE's reliance on very detailed experimental data for the ligands investigated since regression and graphical analysis require equation systems based on experimental data that contain up to 20–30 independent equations. As we are primarily concerned with predicting the properties of ligands that have not yet been synthesised, the intrinsic lack of experimental data all but precludes the application of QALE.

6. The Crabtree scale

Through the efforts of Tolman, Strohmeier and others the electronic properties of monodentate tertiary phosphine ligands were well known by the 1970s and the knowledge could be applied to the design of respective transition metal catalysts [89–93]. However, with the advent of more powerful bidentate chelate ligands in catalysis, the existing $[Ni(CO)_3L]$ scale of Tolman or the other systems like $[CpMn(CO)_2L]$ accumulated by Strohmeier were no longer applicable [94–98]. A scale catering for transition metal carbonyl complexes featuring two phosphine ligands in *cis*-position was needed. This need was addressed by Crabtree when he introduced the *cis*-$[Mo(CO)_4L–L]$ (L–L: bidentate phosphine ligand or two monodentate phosphines) system and correlated it to the existing TEP using the following equation [20]:

$$\nu CO_{Ni} = 0.593\ \nu CO_{Mo} + 871, \qquad R = 0.996 \tag{4}$$

This represents the first time that two scales describing the net donating ability of phosphines were correlated and mutually interconverted. Thus, Crabtree proved Tolman's statement that the choice of transition metal carbonyl system is arbitrary. In principle, any transition metal carbonyl complex for which enough reliable experimental data are available can be used as a valid scale and all the scales can be interconverted since they are based on the same principles.

Indeed, the data do not need to be accumulated experimentally, but can be calculated using adequate theoretical tools, distilled into a scale and the scale calibrated. There is no real need to calibrate the theoretical data with experimental data of the same system, correlating them to TEP is sufficient.

7. Calibration and correlation

As the term implies, a meaningful correlation between two graphs can only be achieved if the one graph is actually related to the other. This can be illustrated by an interesting piece of statistics. In 1960s Sweden both the birth rate and the stork population were in decline. A simple correlation would link the decline of the birth rate with the decrease in stork population. However, to conclude from these data that the stork indeed delivers the babies would be a grave fallacy. With the diverse transition metal carbonyls and nitrosyls described in the present article correlation is clearly permissible. Here, the frequency of the respective A_1 νCO band changes due to the electronic properties of the employed ligand and this change is effected by the interplay of σ-donor ability and π-acceptor strength of the ligand. These ligand properties change the electron density on the central metal and thus the backdonation into the C=O bond. Therefore, the effect on the νCO frequency can be traced back to the same series of phenomena regardless of the transition metal complex employed.

In practical terms, this means that any scale using a transition metal carbonyl complex as the probe and tertiary phosphines as the ligand class to be evaluated can be correlated with any other or with the TEP as the standard system. Taking the argument further, the scale can be extended to other ligand classes such as sulfoxides (Strohmeier) [6,10,29], amines (Cotton) [15,99], *N*-heterocyclic carbenes NHC [100–106], ethers [6,9], arsines and the like [107–109]. With ligands that are themselves σ-donors and π-acceptors like sulfoxides (that behave very similar to tertiary phosphines in many ways), nitriles and isonitriles that is rather obvious and was already described before the introduction of TEP. Other ligands like NHC can be seen as the extension of the trialkyl phosphines beyond the Tolman limit of PBu^t_3 where χ becomes negative and νCO falls below the value of 2056.1 cm^{-1} [110]. This behaviour can be attributed to the excellent σ-donor ability of NHC paired with the almost complete absence of π-acceptor strength associated with this ligand class [111,112]. The other end of the range, i.e. ligands with π-acceptor strength significantly superior to those of phosphites is still largely unexplored, and has become the subject of renewed interest in recent times.

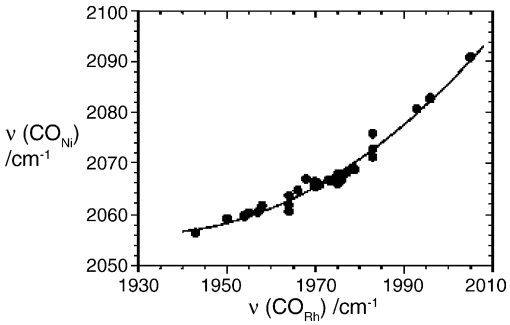

Fig. 1. Correlation between TEP and *trans*-[Rh(CO)ClL$_2$] (reproduced with permission from [115]).

In a recent comparison between Rh-Vaska complexes and [Ni(CO)$_3$L] Otto and Roodt fitted the graph with a simple quadratic equation [21] (Fig. 1). This becomes necessary because the correlation between these two complexes separates into two sections. The first comprises phosphines belonging to the Strohmeier classes I–III and the second to the Strohmeier classes IV–VI. With other words, the electron deficient representatives being good π-acceptors show a different linear correlation then the more electron rich and poor π-acceptor phosphines.

The formulas in this article relating different transition metal conplexes to the TEP scale are only accurate for poor π-acceptors (classes I–III). A good correlation between the TEP scale and the other transition metal complexes used would render an equation different to those given in Table 2. This needs to be taken into account in the prediction of net electron donating ability of electron deficient ligands.

Any correlation of graphs or genesis of a scale from a series of data points is likely to produce data points that are apparently far away from the curve that forms the graph of interest. These data points are often considered as "obvious outliers" and discarded or ignored. However, this procedure is only permissible if there is sufficient reason to assume that this particular data point is the result of erroneous data. It is not permissible to discard a data point simply to improve the correlation factor R as this would amount to altering the experimental result in order to accommodate a theory whereas the prevailing paradigm of science demands the opposite.

There are several reasons why specific data could be erroneous. For instance, the νCO frequencies are solvent dependent [18], dependent on packing effects in the solid state [21], polymorphism in the solid state [113,114] and mistakes in the preparation of the respective complex can result in a compound other than the target molecule [114,115]. In his definition of the TEP, Tolman eliminated most of these causes by defining the conditions of measurement as methylene chloride solutions of the [Ni(CO)$_3$L] complex [18], thereby eliminating all effects associated with solid state and choice of solvent; other raw data have not been selected so carefully. A calibration is performed if a set of calculated data points are correlated with the same data points acquired experimentally. An excellent correlation factor is a prerequisite for accuracy in calibration.

A recent study by Cundari and coworkers is very illustrative [24]. He calculated the A$_1$ band of a series of Rh-Vaska complexes *trans*-[Rh(CO)ClL$_2$]. His data do not correlate well with the experimental data available to him (Fig. 2) [27,91,116–123], but is in good agreement with the Crabtree scale (Fig. 3 and Eq. (5)) [20,124–128]. A recent compilation by Otto and Roodt [21] provides a data set that correlates well with Cundari's findings. The underlying problem is discussed at length by Roodt et al. [21,114,115] and consists of the tendency of *trans*-[Rh(CO)ClL$_2$] to incorporate a third phosphine ligand forming the trigonal bipyramidal complex

Table 1
νCO stretching frequencies of several transition metal carbonyl complexes determined experimentally (cm^{-1})

	TEP	V	Cr	ArCr	MesCr	Mo	f-Mo	f-Mo t	W	Mn	Fe	Fe t	t-Rh	Rh
PhMe$_2$	2067						1935	1937	2071		2041	2051		1970
Ph$_2$Me	2065		2064			2074		1947	2073		2048		1968	1974
Ph	2070	1957	2071	1930	1886	2073	1950		2071	1940	2051	2062	1979	1978
iPr	2062	1948	2059	1919						1928	2030		1950	1960
Cy	2060	1946	2057	1917	1871				2065	1926	2029	2045	1943	1959
m-Tol	2067					2067								1976
OPh	2087	1975	2076	1946	1911	2083	1994	1994	2083	1965		2065		2008
p-Tol	2067	1956				2066			2072	1936	2032		1976	1974
nBu	2064	1950	2062	1921	1876	2070		1928	2067	1930	2028	2045	1955	
Et	2066	1949	2060	1922	1878	2069	1937	1930	2067	1931	2032	2047	1958	
Me	2066	1951		1925	1880	2071	1945	1935	2071	1931		2049	1966	
Bz	2068	1953	2063		1880					1931		2050	1970	
OEt	2077	1964	2071	1934	1891		1971			1945	2044			
OnBu	2078	1965	2071	1936	1892				2079	1945	2054			
OMe	2080	1967	2072	1937	1894	2080	1977	1968	2080	1949	2049	2063		
sBu	2064	1949	2060	1920						1930				
o-Tol	2067	1958	2055			2066			2070	1937	2035		1974	
tBu	2056										2027			

V: [CpV(CO)$_3$L]; Cr: [Cr(CO)$_5$L]; ArCr: [ArCr(CO)$_2$L], Ar: terephthalic acid dimethyl ester; MesCr: [MesCr(CO)$_2$L], Mes: mesitylene; Mo: [Mo(CO)$_5$L]; f-Mo: *fac*-[Mo(CO)$_3$L$_3$] in toluene; f-Mo t: *fac*-[Mo(CO)$_3$L$_3$] in THF; W: [W(CO)$_5$L]; Mn: [CpMn(CO)$_2$L]; Fe: [Fe(CO)$_4$L] in CHCl$_3$; Fe t: [Fe(CO)$_4$L] in toluene; t-Rh: *trans*-[RhCl(CO)L$_2$]; Rh: [Rh(CO)(acac)L].

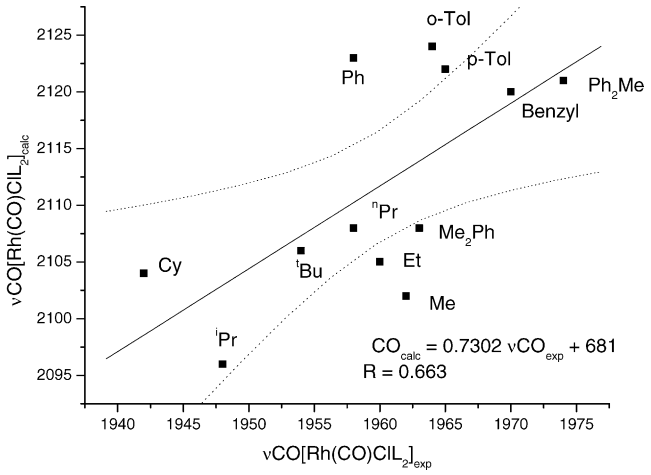

Fig. 2. Correlation between calculated and experimental data for *trans*-[Rh(CO)ClL$_2$]; 95% confidence limit shown by dotted line (cm^{-1}).

[Rh(CO)ClL$_3$]:

$$\nu CO_{Rh} = 1.6863\,\nu CO_{Mo} - 1290, \qquad R = 0.974 \qquad (5)$$

Other reasons comprise the utilization of different solvents or measurement as KBr pellets. Solvent dependency of the νCO frequencies is a known source of error [18], so are packing effects [114] and polymorphism [113,114] in the solid state. An example for this is a quinone for which polymorphism is reported by Fikentscher, displaying a 20–30 cm^{-1} shift for the carbonyl bands [129].

A plethora of transition metal carbonyl complexes was investigated to establish the π-acceptor strength of tertiary phosphine ligands preceding Tolman's introduction of TEP. This wealth of data can be used to correlate the various systems and scales to the TEP. For the convenience of the reader, the available data (Table 1) were correlated to TEP (Table 2) without making any claim as to its completeness.

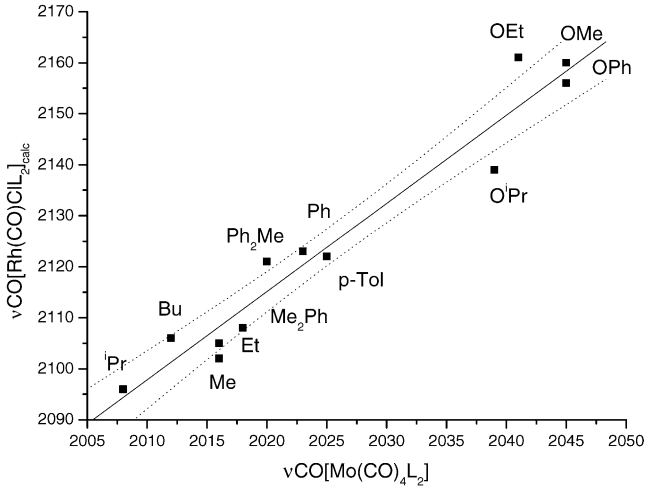

Fig. 3. Correlation of calculated data for *trans*-[Rh(CO)ClL$_2$] with the Crabtree scale; 95% confidence limit shown by dotted line (cm^{-1}).

The correlation between TEP and the experimentally measured data are mostly good (R = 0.926–0.947) to excellent (R = 0.962–0.992). However, some series display a somewhat lower correlation quality (R = 0.799–0.891). This low quality of correlation is caused by phosphines of intermediate π-acceptor strength (Ph$_2$Me, Ph, o-Tol) or phosphites (OMe, OEt, OPh). As has already been discussed, there are usually two independent correlation zones, one for the electron rich and one for the electron poor phosphines. It cannot be surprising that some complexes or metals show a broader correlation window than others.

8. Theoretical methods

For the synthetic chemist, theoretical calculations are useful inasmuch as they enable him to plan the synthesis, to understand the mechanism of the reaction or to predict the properties of the chemicals he is about to prepare. In the present paper we deal with the electronic properties of ligands. From these the properties of the resulting metal complexes are deduced. It is therefore fully sufficient to determine the ligand properties either experimentally or by theoretical means. The most convenient way to determine these properties experimentally has been an indirect method involving transition metal carbonyl complexes. For theoretical studies, this might well prove rather cumbersome and inconvenient as theoretical methods employed to calculate transition metal carbonyl complexes will have to describe the ligand, the metal atom and the interaction between them. Any methods describing only the ligand would therefore be intrinsically more facile.

Thus, a strategy that aims to improve the predictability of the net donating ability of ligands ought to focus on theoretical methods that dispense with the need of transition metals relying exclusively on the ligand itself. However, if the aim were to improve the accuracy with which we can describe a given transition metal, then calculating the TEP on the entire transition metal complex is a very viable approach as there is sufficient experimental data already available for a broad range of transition metals including the "elusive" nickel [24].

So far most theoretical studies were concerned with transition metal complexes rather than just the ligands [24–27,148,149]. A recent paper by Cundari and coworkers [24] is concerned with the reproduction of the A$_1$ νCO frequency of Rh-Vaska complexes *trans*-[Rh(CO)ClL$_2$] (L: tertiary phosphine). In a first step, it aims to reproduce the TEP scale and in a second it concerns itself with the search for bulky electron poor tertiary phosphine ligands, a class of phosphines for which not many representatives have been synthesised.

The most obvious candidate for such theoretical studies is [Ni(CO)$_3$L] itself, the TEP scale. A series of [Ni(CO)$_3$L] complexes has been calculated recently by Clot and coworkers [23] using density functional theory (DFT) at the B3PW91 level. The correlation between experimental and calculated data are excellent, but the expense in terms of computing

Table 2
Correlation between TEP and several experimentally determined series of transition metal carbonyl complexes (cm^{-1})

Complex	Correlation	References
$[CpV(CO)_3L]$	0.885 νCO_V + 338; R = 0.977	[7]
$[Cr(CO)_5L]$	1.075 νCO_{Cr} − 150; R = 0.889	[2,7,130,131,138]
$[ArCr(CO)_2L]$	0.933 νCO_x + 272; R = 0.992	[7]
$[MesCr(CO)_2L]$	0.716 νCO_{Cr} + 720; R = 0.979	[7]
$[Mo(CO)_5L]$	1.116 νCO_{Mo} − 243; R = 0.858	[4,7,132,138,143]
cis-$[Mo(CO)_4(L–L)]$	0.593 νCO_{Mo} + 871; R = 0.996	[20]
fac-$[Mo(CO)_3L_3]$ in toluene	0.359 νCO_{Mo} + 1369; R = 0.985	[4,131,139]
fac-$[Mo(CO)_3L_3]$ in THF	0.358 νCO_{Mo} + 1374; R = 0.962	[146]
$[W(CO)_5L]$	1.334 νCO_W − 696; R = 0.947	[2,7,135–138,142]
$[CpMn(CO)_2L]$	0.711 νCO_{Mn} + 692; R = 0.970	[6,7,31]
$[Fe(CO)_4L]$ in $CHCl_3$	0.576 νCO_{Fe} + 893; R = 0.799	[140,141,144]
$[Fe(CO)_4L]$ in toluene	0.934 νCO_{Fe} + 152; R = 0.891	[7,133,134,145,147]
trans-$[RhCl(CO)L_2]$	0.226 νCO_{Rh} + 1621; R = 0.926	[21,115,140]
[Rh(CO)(acac)L]	0.535 νCO_{Rh} + 1012; R = 0.981	[22]

Ar: terephthalic acid dimethyl ester; Mes: mesitylene; (L–L): two tertiary phosphines or one bidentate chelate phosphine.

time is rather prohibitive for routine predictions of electronic properties of prospective phosphorus ligands.

More time efficient methods are available. Pittard and coworkers have calculated a series of $W(CO)_5L$ and $Mo(CO)_5L$ [25] complexes utilizing the PM3(tm) semi-empirical Hamiltonian, thereby significantly reducing the computing time for each ligand. The correlation with TEP values is very good. However, the method is not reliable for nickel [150]. Hence, theoretical research needed to focus on other systems, preferably incorporating catalyst metals. Cundari and coworkers fulfill this need by embarking on the study concerning *trans*-$[Rh(CO)ClL_2]$ complexes [24]. The study proves that the electronic properties of a prospective phosphorus ligand can be calculated with reasonable effort using Rh-Vaska complexes.

Table 3 shows that data calculated at the PM3(tm) level are less accurate than that calculated at the B3PW91 level of theory, a finding that could be expected. Likewise, experimental data are usually more accurate than calculated one, unless it was calculated at the B3PW91 level. It has to be mentioned though that for the three examples where both theoretical and experimental data are available, the situation is significantly different. Whereas for $[W(CO)_5L]$ and *trans*-$[Rh(CO)ClL_2]$ the R values are almost identical (0.947 and 0.951 for W and 0.926 and 0.914 for Rh), the theoretical data are more accurate than the experimental one in case of $[Mo(CO)_5L]$ (0.952–0.858).

There still remains the question whether DFT methods are indeed necessary. After all νCO stretching frequencies can be calculated from their force constants using simple molecular mechanics models and programmes. A quarter of a century ago, Timney [148] introduced a method to predict the carbonyl stretching frequencies in transition metal compounds based on ligand effect constants. He calculated the force constants with the approximate Cotton–Kraihanzel force field (CKFF) [4,15,17] using a technique known as "energy factoring". Although this approach is very simple [151,152], the results are surprisingly accurate.

Other studies wanted to quantify the σ-donor and the π-acceptor contributions of the ligand, preferably phosphines. In the 1960s, semi-empirical molecular orbital calculations were used to this end [153]. Although computational restrictions did not permit accurate results, these studies paved the way to today's far higher levels of theory. One potent method is the quantitative analysis of ligand effects developed by Giering et al. [27,70,76–78] over the last two decades. QALE relates several physicochemical parameters to the stereoelectronic properties of ligands. Another approach is to systematically analyse the M–P bond length through theoretical calculations exploiting the observation that ligands with good π-acceptor properties display shorter bond lengths than pure σ-donors [149,154–159]. However, the method is not always reliable as the example of the B–P bond shows where the weaker bond can display the shorter bond length [49,50].

But none of these methods meets the ideal criterion of the practical minded chemist to provide a fast and reliable method to calculate directly the electronic properties of the ligand itself.

Table 3
Correlation between TEP and several calculated series of transition metal carbonyls (cm^{-1})

Complex	Correlation	Method	Reference
trans-$[Rh(CO)ClL_2]$	0.3909 νCO_{Rh} + 1238; R = 0.914	PM3(tm)	[24]
$[W(CO)_5L]$	2.016 νCO_W − 2257; R = 0.951	PM3(tm)	[25]
$[Mo(CO)_5L]$	2.110 νCO_{Mo} − 2508; R = 0.952	PM3(tm)	[25]
$[Ni(CO)_3L]$	0.9572 νCO_{Ni} + 4.081; R = 0.996	B3PW91	[23]
$[CpRh(CO)L]$	0.983 νCO_{Rh} + 12.20; R = 0.912	PM3(tm)	[25]
$[Ni(CO)_3L]$	0.880 V_{min} + 2099; R = 0.973	MESP	[28]

9. Molecular electrostatic potential (MESP) [160,161]

It is worth remembering that the TEP is the sum of the σ-donor ability and π-acceptor strength of a given tertiary phosphine. Tolman has used the most basic phosphine known at the time $P(Bu^t)_3$ as the zero point of his scale. He also stated that his corrective factor, the substitution contribution χ_j correlates excellently with the pK_a's of the corresponding phosphonium ions [18]. With other words, there is an excellent correlation between the basicity of a phosphine and its TEP value. Following this argument one only has to calculate the pK_a of an unknown phosphine in order to predict its TEP value. That means that it is principally possible to predict the net donating ability of phosphines without the involvement of transition metal atoms. However, the correlation is not absolute as the pK_a values are subject to a certain steric influence [34,66] experienced by very bulky substituents.

Recently, Suresh and Koga have claimed that the molecular electrostatic potential (MESP) expressed as V_{min} constitutes a method to calculate the νCO value of transition metal carbonyl complexes using the V_{min} to quantify the nucleophilicity of the phosphorus centre [28]. Giering, Prock and Fernandez have refuted this claim [162]. The article by Giering et al. deals mainly with the question whether the MESP correlates correctly to quantities like E^0, ΔH^0 and ΔS^0 in the electrochemical reaction:

$$[Cp(CO)(PR_3)(COMe)Fe]^+ + e^- \rightarrow [Cp(CO)(PR_3)(COMe)Fe]^0 \quad (6)$$

As this paper is concerned with the net electron donating ability of phosphines we will not enter into the discussion and concentrate on the quantities νCO and pK_a instead. As has already been stated previously, an excellent correlation between νCO of $[Ni(CO)_3L]$ and the pK_a of the corresponding phosphonium ion can be demonstrated [18]. Thus, it is sufficient to demonstrate that MESP can be used to calculate the pK_a, if the steric influence on the pK_a is neglected.

The electrostatic potential of a molecule is a real physical property and can be determined experimentally by X-ray diffraction techniques or calculated computationally [163–166]. The MESP has its origin in the charge distribution within the molecule. The backbone is formed by the atoms whose nuclei are the centres of positive charge. The electrons (corresponding negative charge) are distributed around these nuclei occupying their respective orbitals. Thus, local minima V_{min} of the MESP indicate centres of negative charge on the molecule. These are quite frequently electron lone pairs. The absolute value of these minima can serve as a measure for the reactivity of the respective nucleophilic centre and hence for quantities such as the pK_a or the donor ability.

The electrostatic potential $V(r)$ is closely related to the total charge density $D(r)$ through the Poisson equation:

$$\nabla^2 V(r) = -4\pi D(r) \quad (7)$$

and plays a central role in the density functional theory DFT. Therefore, the MESP is not an alternative to DFT dependent theoretical methods, but can be seen as one of the tools in this rapidly growing trade.

In a recent review, Politzer and Murray give a summary on the usefulness of MESP in determining nucleophilic areas and centres in molecules and to quantify their reactivity [163]. Particularly instructive for our purposes are the sections on hydrogen bonding [167–169] and the basicity of amines. Here, the authors demonstrate how the hydrogen bond acceptor strength can be calculated using MESP. As a hydrogen bond acceptor is nothing else but a Brönstedt base, this is equivalent to calculating the pK_a for this nucleophilic centre.

Excellent correlation between measured pK_a's and calculated V_{min} values becomes even more apparent if MESP studies on azines, aliphatic amines, substituted pyridines and aniline derivatives are considered [170,171]. For all these nitrogen containing nucleophiles, the V_{min} for the respective ring or amine nitrogen atoms has been shown to be a good measure for the pK_a.

Having demonstrated that MESP can indeed be used to calculate the pK_a and thus νCO of a nucleophilic ligand, one might be surprised why there shall be a controversy in the literature as to its applicability in determining the net donating ability of phosphines. Suresh and Koga claim excellent correlation between the V_{min} of a phosphine and the frequency of the νCO band of the corresponding transition metal carbonyl complex [28]. Giering et al., however, claim that such a correlation is not permissible since one can distinguish three families of phosphines (alkyl, aryl and phosphite) that each correlate separately with the respective νCO band [162].

A full QALE analysis [162] on the MESP data provided by Suresh and Koga [28] reveals inaccuracies in E^0 and ΔH^0 due to dependencies of these parameters on τ, E_{ar}, and π_p not accounted for by the MESP method employed. If, however, the correlation with TEP is investigated and this correlation lies at the heart of the present review article, one detects three closely spaced parallel lines roughly representing the first three ligand classes described by Strohmeier. Treating the data as one straight line introduces a systematic, but fairly small, error that by no means invalidates the whole method. Thus, the utility of MESP does not lie in the replacement of existing methods based on available experimental data, but in the easy, fast and inexpensive method of collecting data for uncommon or unknown ligands. The trade off is a certain inaccuracy in the net electron donation value for individual ligands. As the correlation between TEP and the MESP is high despite its theoretical shortcomings, this is more than acceptable.

10. Relation to other parameters

The article by Clot and coworkers [23] discusses the correlation of their computationally derived ligand electronic

parameter CEP with the TEP, the Lever electronic parameter LEP [172,173] and the Hammett parameter σ_m. The LEP is based on the electrochemical E^0 value for various redox couples where the transition metal complex comprises the ligand of interest. The Ru(III)/Ru(II) couple is the best known example. The Hammett parameters describe the substituent dependent change of acidity in *o*-, *m*-, *p*-substituted benzoic acids, respectively.

Clot et al. were surprised to find an excellent correlation between the CEP (TEP) and the σ_m Hammett parameter. This excellent correlation is maybe not so very surprising if one considered that Tolman already found that the TEP correlates very well to the pK_a values of the corresponding phosphonium ions and that the definition of the Hammett parameter is closely related to the pK_a value of the defining substances. The MESP has also been used to calculate the σ_i—Hammettt Parameters via RACEL [174,175] supporting Suresh and Koga's claim that the MESP can be used to calculate TEP. The correlation of CEP (TEP) to LEP was found to be only modest ($R = 0.91$).

Given the correlations of TEP to LEP and σ_m via the CEP found by Clot et al., it becomes clear that V_{min} values of the MESP can be used to calculate a far broader range of ligands than tertiary phosphines utilizing the correlation links existing between TEP, LEP, σ_m, pK_a and V_{min} given by Clot's CEP.

11. Conclusion

The experimentally determined Tolman electronic parameter is still the universally accepted method to measure the net donating ability of a tertiary phosphine. Although it is based on monodentate phosphines by its defining complex [Ni(CO)$_3$L], it can be used to measure chelate ligands by employing related complexes like *cis*-[Mo(CO)$_4$L–L] [20].

Attempts to calculate the TEP using theoretical methods were successful on the B3PW91 level. On the less sophisticated level PM3(tm) these attempts failed for nickel, but were successful for other metals like tungsten ([W(CO)$_5$L]), molybdenum ([Mo(CO)$_5$L]) and rhodium (*trans*-[CpRh(CO)L$_2$Cl]), although correlation for rhodium is significantly worse than for molybdenum and tungsten. All these methods produce values for A_1 that are 5–10% above the experimental ones. Other methods include modified CKFF studies and bond length calculations.

It is not necessary to employ transition metal complexes for the calculation of the net donating ability of tertiary phosphines as it is possible to calculate their TEP directly from their own MESP. The correlation with TEP is always very good. However, for B3PW91 calculations it is significantly better than for PM3(tm). The least effort in terms of required software, hardware and computer time is required by the MESP approach as it does not involve the calculation of a transition metal in addition to the ligand and can be performed on a more basic level than the others. However, with today's improvements in computer power at the PC level, these differences are rapidly becoming irrelevant.

Thus, the choice of theoretical method rests with the investigator and is open to choice dependent on such criteria as individual preferences, software availability, or locally existing routines and knowhow.

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