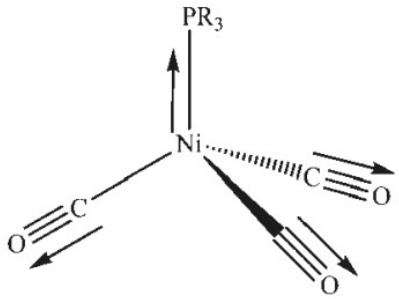

Figure 30. The A_1 stretch of $Ni(CO)_3L$ used to determine the TEP in metal-phosphine complexes.

Upon coordination to a metal, ν(CO) typically decreases from 2143 cm^{-1} of free CO. This can be explained by π backbonding i.e. the metal is able to form a π-bond with the carbonyl ligand by donating electrons through its *d*-orbitals into the empty antibonding π^* orbitals on CO. This increases the strength of metal–carbon bond, but also weakens the bond between carbon and oxygen. Moreover, the C–O bond is further weakened if other ligands present increase the π-electrons-density on the metal centre, and ν_{CO} decreases. However, if other ligands compete with CO for π backbonding, ν_{CO} would increase. Tolman analysed a series of seventy ligands in reference to $P(t\text{-}Bu)_3$, because three t-butyl groups make it as the strongest donor ligand. Consequently, the A_1 absorption band of carbonyl ligands in $Ni(CO)_3[P(t\text{-}Bu)_3]$ complex appears at the lowest wavenumber (2056.1 cm^{-1}), which is obviously due to the largest magnitude of back-bonding among all phosphines. Based on these observations, Tolman proposed a parameter χ_i to show the effect of individual substituents (R, R′, R″) on this band as accorded by equation (2):

$$\nu_{CO} = 2056.1\ \text{cm}^{-1} + \sum_{i=1}^{3} \chi_i\ \text{cm}^{-1} \tag{2}$$

Now the calculation of value of χ_i for each individual substituent in symmetrical phosphines can be done just by putting their observed spectral band. Let's say, we want to calculate the Tolman electronic parameter for PCl_3. The infrared absorption of A_1 symmetry for $Ni(CO)_3(PF_3)$ is observed at 2097.0 cm^{-1}. On putting this value for ν_{CO} in the equation (2), we get:

$$2097.0\ \text{cm}^{-1} = 2056.1\ \text{cm}^{-1} + \sum_{i=1}^{3} \chi_i\ \text{cm}^{-1} \tag{3}$$

$$2097.0\ \text{cm}^{-1} = 2056.1\ \text{cm}^{-1} + 3 \times \chi_i(\text{Cl})\ \text{cm}^{-1} \tag{4}$$

$$\chi_i = 14.8\ \text{cm}^{-1} \tag{5}$$

The values of χ for different substituents are listed in the Table 4; which in turn can easily be used to calculate the theoretical position of A_1 absorption band in case of tertiary phosphine ligands in which R, R′, and R″ are not the same anymore.

Table 4. Substituent χ Factors for Phosphine and Related Ligands.

Substituent	χ_i (cm^{-1})	Substituent	χ_i (cm^{-1})
–*t*Bu	0.0	–OEt	6.8
–Cyclohexyl	0.1	–OMe	7.7
–*i*Pr	1.0	–H	8.3
–Et	1.8	–OPh	9.7
–Me	2.6	$-C_6H_5$	11.2
–Ph	4.3	–Cl	14.8
$-p$-C_6H_4F	5.0	–F	18.2
$-m$-C_6H_4F	6.0	$-CF_3$	19.6

The Tolman electronic parameter (TEP) and the ligand cone angle are used to characterize the electronic and steric profile of phosphines, which are very popular ligands for catalysts.