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Bonding and energetics of phosphorus(III) ligands in transition metal complexes

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CONTENTS

ABSTRACT

Thermochemical data for transition metal complexes containing phosphorus(III) ligands have been reviewed and used to derive and discuss metal–phosphine and metal–phosphite bond dissociation enthalpies. The survey is preceded by brief overviews of the nature of the M—P bond and of the steric and electronic properties of the phosphorus ligands. Also included is a critical survey of thermochemical data of phosphines and phosphites.

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1. INTRODUCTION

Tertiary phosphorus ligands play a central role in the organometallic chemistry of transition metals (see, for example, refs. 1 and 2). The number of phosphines and phosphites that bind to transition metals is immense, displaying a wide range of steric and electronic effects. Probably more than any other ligand, phosphines and phosphites have been used to change and control the reactivity of transition metal complexes in reactions of synthetic interest, or to improve the activity and the selectivity of catalysts. The cleavage of a metal–phosphorus(III) bond, M—P, to form a coordinatively unsaturated species is a key step in many of those reactions. Thermochemical data on metal–phosphorus(III) bonds are therefore of fundamental importance in understanding and predicting possible reaction pathways. Moreover, these data can be used to assess results of theoretical calculations.

The main purpose of this review is to provide a critically analyzed data bank on the energetics of the metal–phosphorus(III) bonds. This is presented in Sect. 4 and preceded by brief descriptions of the nature of the M—P bond (Sect. 2), and the steric and electronic properties of phosphorus(III) ligands (Sect. 3). Section 4 also includes a critical survey of the enthalpies of formation of phosphines and phosphites.

The literature was reviewed until the end of 1991, but an effort was made to include work published in 1992.

2. THE TRANSITION METAL–PHOSPHORUS(III) BOND

The transition metal–phosphorus(III) bond is traditionally viewed as a result of two different contributions [1,2]: electron donation from the phosphorus lone pair orbital to an empty metal orbital of appropriate symmetry, leading to a σ interaction, and back-donation from filled metal orbitals to vacant ligand orbitals, leading to a π interaction. The existence of metal-to-ligand π back-bonding and the relative magnitudes of the σ and π components have been investigated by several theoretical methods [3–7], and by an array of experimental techniques including X-ray crystallography [8–17], IR [8,18–25], NMR [8,26–29], UV–Vis [8,30–32], electron transmission [33], photoelectron [34–38], and Mössbauer spectroscopies [39], as well as electrochemical methods [40,41], and paramagnetic susceptibility [30,42] and pK_a [43,44] measurements.

Results of X_α and ab initio molecular orbital calculations on simple phosphines, PR_3 (R = H, F, Cl, Me), and their complexes with Cr or Ni [3–7] indicate that σ and π interactions are always present. Contrary to the conventional view which ascribes the π acceptor properties of phosphorus ligands to empty phosphorus 3d orbitals, these calculations indicate that the π acceptor orbital (LUMO) in the PR_3 ligand has some P—R σ^* character [5,6] and that the largest contribution to this LUMO comes from the P 3p orbitals [4,5,7]. The contribution of the P 3d orbitals to π back-bonding is, however, relevant, considerably increasing the π acceptor capability of the ligand (mixing the phosphorus 3d and the P–R σ^* orbitals gives an hybrid orbital better suited, both by energy and overlap criteria, for electron acceptance from the transition metal) [6,7]. The relative contributions of the P 3d and P 3p orbitals to the ligand acceptor orbital vary with the substituent R. For example, it has been predicted that the ratio of the contributions 3d/3p equals 0.6, 0.7 and 0.5, for PH_3, PMe_3 and PF_3, respectively [4]. An important contribution to the binding from electrostatic interactions between the metal and the ligand dipole was also found in the case of the $Ni(PH_3)$ fragment [6]. The balance between the σ and π interactions depends on the electronegativity of the substituents bonded to the phosphorus atom. For example, it has been found that PCl_3 is a poorer π acceptor and somewhat better σ donor than PF_3 [7(b)], and that in $Ni(PH_3)$ the σ interaction strongly dominates over the π interaction [6]. This effect is related to the fact that electronegative substituents, such as fluorine, increase the P 3p character in the ligand acceptor orbital, lowering its energy, and improve its directionality towards the metal, thus enhancing the π back-bonding effect [4,5,7]. Therefore, highly polar bonds such as those between phosphorus and fluorine have low-lying σ^* orbitals with appropriate symmetry for overlap with metal d orbitals, and are better π acceptors than, for example, the P–H σ^* orbitals which are higher in energy. Furthermore, because the P–F bond is highly polar towards the fluorine atom, the σ^* orbital must necessarily be highly polar towards the phosphorus atom, thus increasing the σ^*-metal dπ overlap [5].

The conclusion that the metal–phosphorus π bond occurs through orbitals that are essentially P–R σ^* has received support from results of electron transmission spectroscopy and X-ray crystallography. Electron transmission spectroscopy (ETS) measures the energy of formation of a negative ion arising from electron capture into an unoccupied orbital, and can give information about the energy of the LUMO of the molecule investigated [33]. Using ETS, Giordan and co-workers [33] found that the energy of the LUMO in PR_3 ligands is very sensitive to the R group, suggesting that this orbital is best described as a P–R σ^* molecular orbital rather than a P 3d atomic orbital.

Orpen and Connelly [16(a)] examined the molecular structures of a number of transition metal complexes that form redox couples, and observed that oxidation leads to an increase of the M–P bond distance and a decrease of the P–R bond distance. These observations are consistent with the theoretical prediction that the M–P bond involves orbitals that are partially P–R antibonding, and that the π interaction is generally important for bonding of phosphorus(III) ligands to transition metals that are not in high oxidation states. Oxidation reduces the ability of a metal to back-donate electron density to the PR_3 ligand. As a consequence, the P–R σ^* orbital becomes less populated and the P–R bond distance decreases. The increase of the M–P bond length reflects the weakening of this bond caused by the loss in π back-bonding interaction. Orpen and co-workers have recently extended the study of the transition metal–phosphorus(III) bond by analyzing the geometry variations in a very large number of ZPR_3 fragments, where PR_3 is a phosphine and Z may be a transition metal or a main group element [16(b)]. The results of this analysis indicate that coordination of PR_3 to transition metals (where the potential for π back-bonding exists) leads to geometries with smaller R–P–R angles and longer P–R distances than in fragments where Z is a pure σ acceptor, such as H^+. Moreover, the R–P–R angle increases and the P–R distance decreases on moving from Cr to Cu, Ru to Ag, and Re to Au across the transition series. The trend is reversed to the left of the Periodic Table, i.e. the R–P–R angle increases from Cr to V, from Ru to Mo, and from Re to W. These observations have been interpreted using a qualitative molecular orbital model consistent with the results of the theoretical methods referred above [16]. According to this model, σ donation results mainly in a depopulation of the lone pair orbital, which leads to an increase of the R–P–R angle. The increase of the R–P–R angle improves the overlap between the P $3p_x$ and $3p_y$ orbitals and the R group σ orbitals involved in the P–R σ bond and this is reflected in the shortening of the P–R bond. On the other hand, coordination of the phosphorus(III) ligand to a π donor species will partially populate the PR_3 LUMO which becomes more stabilized as the R–P–R angle closes. Thus, an increase of the π back-bonding interaction leads to a decrease of the R–P–R angle. The increase of the π back-bonding interaction also weakens the P–R bond since, as indicated above, the π acceptor orbital of the phosphine has P–R σ^* character. The increase of the R–P–R angle and the decrease of the P–R bond distance in the series Cr to Cu, Ru to Ag, and Re to Au suggests that the metal π back donation ability is decreasing from left to right in those series, probably due to the fact that the metal d electrons are becoming more tightly bound. According to Orpen and co-workers [16(b)], this trend is not expected to hold for complexes of high oxidation state early transition metals in which the number of d electrons is low or even zero, and the σ interaction dominates. The inversion that occurs at V, Mo, and W may reflect such behaviour [16(b)].

In summary, the theoretical and experimental research on the nature of the transition metal–phosphorus(III) bond has generated a large body of results from which a consensus seems to be emerging that the synergic model involving $PR_3 \rightarrow M$ σ donation and $M \rightarrow PR_3$ π back-donation is adequate to describe the transition metal–phosphorus(III) bond. It is also generally agreed that σ donation involves a ligand orbital which is mainly associated to the phosphorus lone pair, and the π back-donation essentially involves the P–R σ^* orbital rather than the pure P 3d orbital. The relative importance of the σ and π components in determining the M–P bond for different phosphines and phosphites is, however, still a matter of debate. This problem has been intensively studied using various experimental methods and the conclusions of these studies often depend on the technique used and on the systems chosen. For example, the structural studies by Orpen and Connelly [16(a)] of complexes that form redox couples, referred to above, suggest that π-back bonding is generally important in determining the transition metal–phosphorus bond. The energy splittings between the metal-based ionizations in $Mo(CO)_5L$ complexes ($L = PMe_3$, PEt_3, PBu_3, and the diphosphines $Me_2PCH_2PMe_2$ and $Me_2PCH_2CH_2PMe_2$ acting as monodentate ligands) measured by photoelectron spectroscopy indicate that the π-back bonding ability is the same for all the phosphines studied and is about 25% that of CO [38]. The $Mo(CO)_5L$ complexes and/or the complexes studied by Orpen and Connelly, however, include phosphines such as PEt_3 and $P(t\text{-}Bu)_3$, which have been classified by Giering and co-workers as pure σ donors (regardless of the metal), based on correlations involving bond distances, reaction enthalpies, CO stretching frequencies, pK_a values, reduction potentials, etc. [17,44].

3. STERIC AND ELECTRONIC PROPERTIES OF PHOSPHORUS(III) LIGANDS

A considerable number of studies have been devoted to the quantification of the electronic and stereochemical characteristics of phosphorus(III) ligands, and several scales of relative "σ donor/π acceptor strength" and "stereochemical bulkiness" have been proposed. These scales have been widely used to define strategies of synthesis and are also important to this review because the M—P bond dissociation enthalpies reflect the electronic and stereochemical properties of the phosphorus ligands. The most representative approaches used are discussed in this section.

3.1 *Steric properties of phosphorus(III) ligands*

The stereochemical characteristics of phosphorus(III) ligands have been quantified essentially on the basis of four geometrical concepts: the cone angle, the solid angle, the ligand profile, and the solid angle factor [2,45–60].

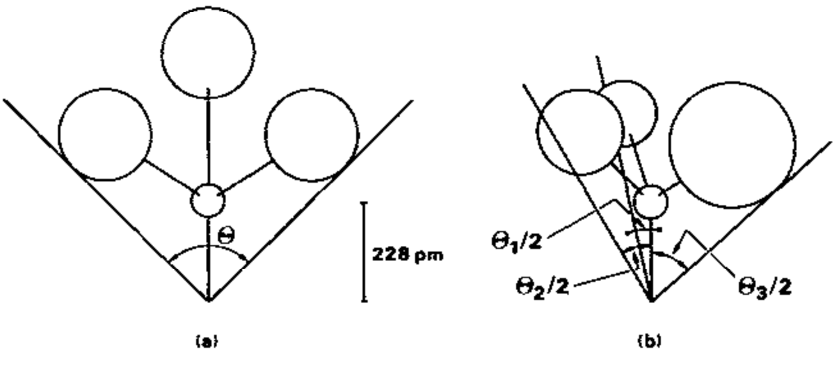


Fig. 1. The cone angle for (a) symmetrical and (b) unsymmetrical ligands (adapted from ref. 46(b)).

TABLE 1

Cone angles for phosphorus(III) ligands

Molecule[a]	θ[b] (degrees)	Molecule[a]	θ[b] (degrees)
PR_3		P(*p*-Tol)$_3$	145
		P(*p*-C_6H_4OMe)$_3$	145[p]
PH_3	87	P(*p*-$C_6H_4NMe_2$)$_3$	145[p]
	91[h]	PBz_3	165
PF_3	104		130[e]
PCl_3	124		139[e]
PBr_3	131		160[j]
$P(CF_3)_3$	137	P(mesityl)$_3$	212
	128[f]	P(1-naphthyl)$_3$	200[e]
PMe_3	118	P(biphenyl)$_3$	200[e]
	<117[c]	$P(OMe)_3$	107
	137[b]		<117[c]
PEt_3	132		128[d]
	166[h]	$P(OEt)_3$	109
	137[d]		<117[c]
$P(CH_2CH_2CN)_3$	132		110[i]
	129[c]		134[d]
$P(C_3H_5)_3$	125[e]	$P(OCH_2CH_2Cl)_3$	110
	132[n]		<117[c]
PPr_3	132	P(O–i-Pr)$_3$	130
	139[j]		124[c]
P(i-Pr)$_3$	160	$P(OBu)_3$	112[i]
	164[c]		109[n]
PBu_3	132	P(O-*t*-Bu)$_3$	172
	127[c]	$P(OCy)_3$	141[o]
	136[p]		128[c]
P(i-Bu)$_3$	143	$P(OPh)_3$	128
P(s-Bu)$_3$	160		123[c]
P(*t*-Bu)$_3$	182	P(O–*p*-C_6H_4Cl)$_3$	128[n]
P(*neo*-Pe)$_3$	180	P(O–*o*-Tol)$_3$	141
PCy_3	170		128[c]
	173[c]	P(O–*p*-Tol)$_3$	128
POc_3	132[e]	P(O–*o*-C_6H_4-i-Pr)$_3$	148
PPh_3	145	P(O–*o*-C_6H_4-*t*-Bu)$_3$	175
	159[c]	P(O–*o*-C_6H_4Ph)$_3$	152
$P(C_6F_5)_3$	184	P(O–2,6-$C_6H_3Me_2$)$_3$	190
P(*m*-C_6H_4F)$_3$	145	$P(OMen)_3$	140
P(*p*-C_6H_4F)$_3$	145[p]	$P(NCH_2CH_2)_3$	108
P(*m*-C_6H_4Cl)$_3$	165[n]	$P(NMe_2)_3$	157
P(*p*-C_6H_4Cl)$_3$	145[p]		
P(*p*-$C_6H_4CF_3$)$_3$	145[p]	*PRR'_2*	
P(*o*-Tol)$_3$	194		
P(*m*-Tol)$_3$	165[p]	$PHMe_2$	118[h]

TABLE 1 (*continued*)

Molecule[a]	θ[b] (degrees)	Molecule[a]	θ[b] (degrees)
$PHEt_2$	137[h]	PPh_2Pr	141[c]
$PH(CH_2CH_2CN)_2$	117[o]		143[l]
$PH(i\text{-}Pr)_2$	148[h]	$PPh_2(i\text{-}Pr)$	150
$PHCy_2$	142[m]		132[e]
	143[o]	PPh_2Bu	140[c]
$P(CF_3)Me_2$	124		141[c]
$PMeH_2$	105[h]		143[j]
$PMe(i\text{-}Bu)_2$	135[o]	$PPh_2(t\text{-}Bu)$	157
$PMeCy_2$	153[e]	PPh_2Pe	145[j]
$PMe(p\text{-}C_6H_4Cl)_2$	136[c]	PPh_2Hex	141[e]
$PMe(p\text{-}Tol)_2$	136[e]		145[j]
$PMe(OEt)_2$	112[o]	PPh_2Cy	153[m]
$PEtH_2$	111[h]	$PPh_2(C_6F_5)$	158
$PEt(OMe)_2$	115	$PPh_2(o\text{-}Tol)$	161[e]
$P(C_3H_5)Cy_2$	155[c]	PPh_2Bz	143[e]
$PPr(t\text{-}Bu)_2$	165[e]		152[p]
$P(i\text{-}Pr)H_2$	116[h]	$PPh_2(OMe)$	132
$P(i\text{-}Pr)Men_2$	209[g]		129[c]
$P(t\text{-}Bu)H_2$	118[h]	$PPh_2(OEt)$	133
$P(t\text{-}Bu)Me_2$	139[e]	$PPh_2(OPr)$	140[j]
$P(t\text{-}Bu)Et_2$	149[c]	$PPh_2(OBu)$	145[l]
$P(t\text{-}Bu)Pr_2$	149[e]	$PPh_2(OPh)$	139[j]
$P(t\text{-}Bu)(i\text{-}Pr)_2$	167[c]	$PPh_2(o\text{-}C_6H_4OMe)$	170[p]
$P(t\text{-}Bu)Bu_2$	149[e]	$PPh_2(NEt_2)$	160[l]
$P(t\text{-}Bu)(p\text{-}Tol)_2$	157[e]	$PPh_2(SiMe_3)$	162[j]
$P(t\text{-}Bu)Cy_2$	174[c]		
	171[i]	*$PPhR_2$*	
$P(o\text{-}Tol)H_2$	113[h]		
$P(p\text{-}Tol)Me_2$	127[c]	$PPhH_2$	101
$P(p\text{-}Tol)(t\text{-}Bu)_2$	170[e]		106[h]
$P(p\text{-}C_6H_4Cl)Me_2$	127[e]	$PPhCl_2$	131[p]
$P(p\text{-}C_6H_4OMe)Me_2$	127[c]	$PPhMe_2$	122
			125[c]
PPh_2R			142[h]
			127[i]
PPh_2H	128	$PPhEt_2$	136
	126[p]	$PPh(C_2H_3)_2$	122[e]
PPh_2Cl	137[p]	$PPh(CH_2CH_2CN)_2$	136[o]
PPh_2Me	136	$PPh(C_3H_5)_2$	132[e]
	132[c]	$PPhPr_2$	136[c]
PPh_2Et	140		141[l]
	141[j]	$PPh(i\text{-}Pr)_2$	155[j]
$PPh_2(C_2H_3)$	133[e]	$PPh(1\text{-}butenyl)_2$	132[e]
$PPh_2(CH_2CH_2CN)$	141[o]	$PPhBu_2$	136[e]
$PPh_2(C_3H_5)$	138[e]		141[l]

TABLE 1 (*continued*)

Molecule[a]	θ[b] (degrees)	Molecule[a]	θ[b] (degrees)
$PPh(t\text{-}Bu)_2$	170	*Other*	
$PPhPe_2$	136[e]		
	143[l]	PPhHMe	120[h]
$PPhHex_2$	136[e]	PPhHEt	130[h]
	145[l]	$Me_2PCH_2CH_2PMe_2$	107
$PPhCy_2$	162[k]	$Et_2PCH_2CH_2PEt_2$	115
$PPh(o\text{-}Tol)_2$	177[e]	$Cy_2PCH_2CH_2PCy_2$	142
$PPhBz_2$	141[e]	$Ph_2PCH_2PPh_2$	121
$PPh(OMe)_2$	115	$Ph_2PCH_2CH_2PPh_2$	125
	125[c]	$Ph_2P(CH_2)_3PPh_2$	127
	120[p]	$P(OCH_2)_3CR$	101
$PPh(OEt)_2$	115		<117[c]
	116[l]	$P(CH_2O)_3CR$	114
	116[j]	 **1**	106
	121[p]		
$PPh(OPr)_2$	120[l]		
$PPh(OBu)_2$	118[j]	 **2**	102[k]
	123[l]		
$PPh(OPh)_2$	134[i]		
	129[j]		
$PPh(OMen)_2$	142[i]		
$PPh(SiMe_3)_2$	175[l]		

[a] Bz = benzyl; Cy = cyclohexyl; Hex = hexyl; Oc = Octyl; Pe = pentyl; Tol = tolyl; Men = menthyl. [b] Data from Ref. 46, unless stated otherwise. [c] Ref. 50. [d] Ref. 49. [e] Ref. 47(b). [f] Ref. 16(b). [g] Ref. 48. [h] Ref. 51. [i] Ref. 52. [j] Ref. 53. [k] Ref. 54. [l] Ref. 47(a). [m] Ref. 55. [n] Ref. 44(b). [o] Ref. 44(c). [p] Ref. 44(d).

3.1.1 *The cone angle*

The cone angle, θ, was introduced by Tolman [46] to explain the ability of phosphorus ligands to compete for coordination positions on Ni(0) complexes based on equilibrium (1) (L, L′ = phosphine or phosphite) in toluene.

$$NiL_4(soln) + nL'(soln) = NiL_{4-n}L'_n(soln) + nL(soln) \tag{1}$$

According to Tolman's definition, the cone angle for symmetric ligands (Fig. 1(a)) is "the apex angle of a cylindrical cone, centred 228 pm from the centre of the P atom, which just touches the van der Waals radii of the outermost atoms of the ligand" [46]. For an unsymmetrical ligand $PR_1R_2R_3$ (Fig. 1(b)), the cone angle is calculated from the equation

$$\theta = \frac{2}{3}\sum_{i=1}^{3}\frac{\theta_i}{2} \tag{2}$$

where θ_i represents the angle of the corresponding symmetric $P(R_i)_3$ phosphines or phosphites. In the case of chelating diphosphines, $\theta_i/2$ is the angle between one M–P bond and the bisector of the P–M–P angle.

The cone angle was, to a first approximation, measured by using molecular Corey–Pauling–Koltum (CPK) space-filling models. Tolman chose the conformation giving the minimum cone angle if more than one conformation was possible for the ligand. The values obtained were then reanalyzed, using a correlation between θ and the equilibrium constant of reaction (3), K_d, in which the steric effects appear to dominate over the electronic effects.

$$\mathrm{NiL_4(soln)} \overset{K_d}{\rightleftharpoons} \mathrm{NiL_3(soln)} + \mathrm{L(soln)} \tag{3}$$

If equilibrium (3) is controlled by steric effects, K_d should increase with θ and, for example, deviations observed from this trend led Tolman to change the cone angle of $P(O\text{-i-Pr})_3$ from 114 to 130°. The ligand cone angles for a variety of phosphines and phosphites recommended by Tolman [46] are listed in Table 1.

Tolman's data bank has been reassessed and extended by several authors based on structural arguments, results of MINDO/3 calculations, and different types of correlation [47–55]. These results are also included in Table 1.

3.1.2 *The solid angle*

The concept of cone angle proposed by Tolman does not account for the variation in steric demand as the orientation of the ligand changes about the M–P bond. This concept is not adequate to describe, for example, the stereochemical characteristics of bulky phosphines in crowded complexes such as $Pt(PCy_3)_3$ [56]. In this case, the cyclohexyl ligands adopt stable configurations that correspond to a

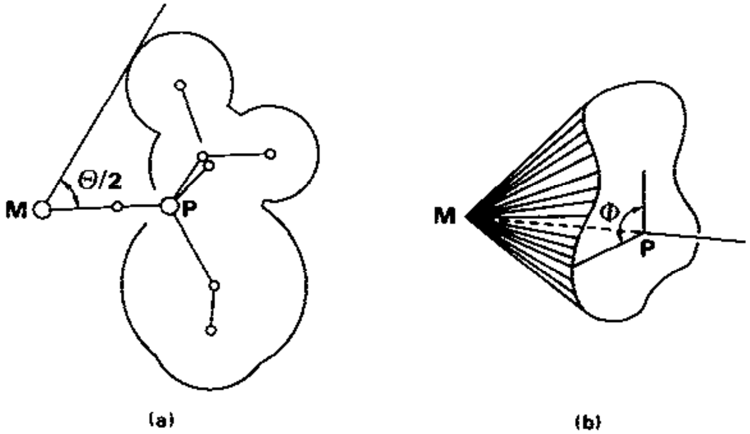


Fig. 2. The solid angle for triethylphosphine (adapted from ref. 48).

TABLE 2

Solid angles for phosphines[a,b]

L	Complex	Ω[c]	Θ[c] (degrees)
PR_3			
PEt_3	*trans*-$Pd(H)(Cl)L_2$	3.60	129.5
		3.72	131.8
PEt_3	PtL_4	3.09	118.9
		3.14	119.9
$P(i\text{-}Pr)_3$	$Ir(H)(C_4H_6)L_2$	3.89	135.2
		3.96	136.7
$P(i\text{-}Pr)_3$	$Ir(C_3H_5)L_2$	4.02	137.8
PCy_3	PdL_2	4.48	146.7
PCy_3	*trans*-$Pt(H)_2L_2$ (monoclinic)	4.61	149.1
PCy_3	*trans*-$Pt(H)_2L_2$ (triclinic)	4.40	145.0
PCy_3	PtL_3	4.18	140.6
PPh_3	$Co(CO)_2(NO)L$	3.58	129.0
PPh_3	$[Cu(Cl)L]_2$	3.57	128.8
PPh_3	$Cu(Cl)L_3$	3.70	131.5
PPh_3	$[CuL_3]^+BF_4^-$	3.77	132.9
PPh_3	$Ru(H)_2L_4$	3.31	123.5
		3.32	123.7
		3.35	124.4
		3.38	124.9
PPh_3	$Rh(Cp^*)(C_2H_4)L$	3.54	128.2
PPh_3	PdL_4	3.44	126.2
		3.43	125.9
PPh_3	$Ir(NO)L_3$	3.59	129.2
PPh_3	*cis*-$Pt(Cl)(DTT)L_2$	3.82	133.8
		3.72	131.8
PPh_3	$Au(Cl)_3L$	3.75	132.4
PRR'_2			
$P(i\text{-}Pr)Men_2$	PdL_2	6.09	176.5
PPh_2R			
PPh_2Me	MoH_4L_4	2.99	116.7
		2.99	116.8
		3.05	118.1
		3.10	119.1
PPh_2Me	$[IrL_4]^+BF_4^-$	3.31	123.4
		3.27	122.6
PPh_2Me	$[AuL_2]^+PF_6^-$	3.44	126.2

TABLE 2 (*continued*)

L	Complex	Ω^c	Θ^c (degrees)
$PPhR_2$			
$PPhMe_2$	*cis*-$Pd(Cl)_2L_2$	2.90	125.0
$PPhMe_2$	$[Ir(CO)_3L_2]^+ClO_4^-$	3.06	118.3
		3.03	117.7
$PPhMe_2$	PtL_4	2.82	113.1
		2.81	113.1
		2.79	112.4
		2.88	114.6
$PPh(t\text{-}Bu)_2$	PdL_2	4.94	155.3
$PPh(t\text{-}Bu)_2$	$Pt(Cl)_2L_2$	4.61	149.1
		4.50	147.0

[a] DTT = di-*p*-tolyltriazenido; Men = menthyl.

[b] Ref. 48.

[c] See text.

considerable interpenetration of their cone angles and on the basis of $\theta(PCy_3) = 170°$ (Table 1) the complex $Pt(PCy_3)_3$ would be expected to be unstable [56]. Immirzi and Musco [48] introduced the use of the solid angle Ω to account for the variation in stereochemical demands of a phosphine or phosphite as a function of its orientation relative to the M—P bond. This concept is illustrated in Fig. 2. For each orientation of the ligand about the M—P bond, characterized by an angle ϕ, a planar Tolman cone angle $\theta/2$ is defined by the tangent to the van der Waals radii of the outermost atom of the ligand (Fig. 2(a)). The set of $\theta/2$ values corresponding to the variation of ϕ from 0 to 360° generates a non-circular cone (Fig. 2(b)) whose solid angle, Ω, is mathematically defined by eqn. (4). The first integral in eqn. (4) generates the planar semi-cone $\theta/2$. The second integral corresponds to the rotation of this semi-cone over 2π. Note that eqn. (4) relates the solid angle Ω with the Tolman cone angle θ for each conformation of the ligand. Based on X-ray data, and assuming a constant M—P distance of 230 pm, Immirzi and Musco calculated solid angles for a number of phosphines bonded to different metals [48]. These data are summarized in Table 2. The results in Table 2 show that, in general, if several crystallographically independent ligands of the same species are present in the same complex (possibly with different conformations) the solid angles Ω are very similar [48]. Among the complexes containing the same ligand, Ω decreases if the crowding around the metal increases [48]. Immirzi and Musco have also derived the equivalent of Tolman's cone angle for a circular cone corresponding to a solid angle Ω (eqn. (5)). This angle, Θ, is also listed in Table 2. The Θ values are systematically lower than the corresponding Tolman's θ (Table 1), in particular for the bulkiest ligands [48].

$$\Omega = \int_0^{\theta/2} \int_0^{2\pi} \sin\theta \, d\theta \, d\phi = 2\pi[1 - \cos(\theta/2)] \tag{4}$$

$$\Theta = 2 \operatorname{arcos}[1 - (\Omega/2\pi)] \tag{5}$$

3.1.3 *The ligand profile*

The problem of ligand intermeshing has also been approached using the ligand profile concept [57(a),58] illustrated in Fig. 3. The ligand profile is generated in exactly the same way as a solid angle (Fig. 2(a)). First, the angle $\theta/2$ subtended by the M–P bond and the line r tangent to the van der Waals radii of the outermost

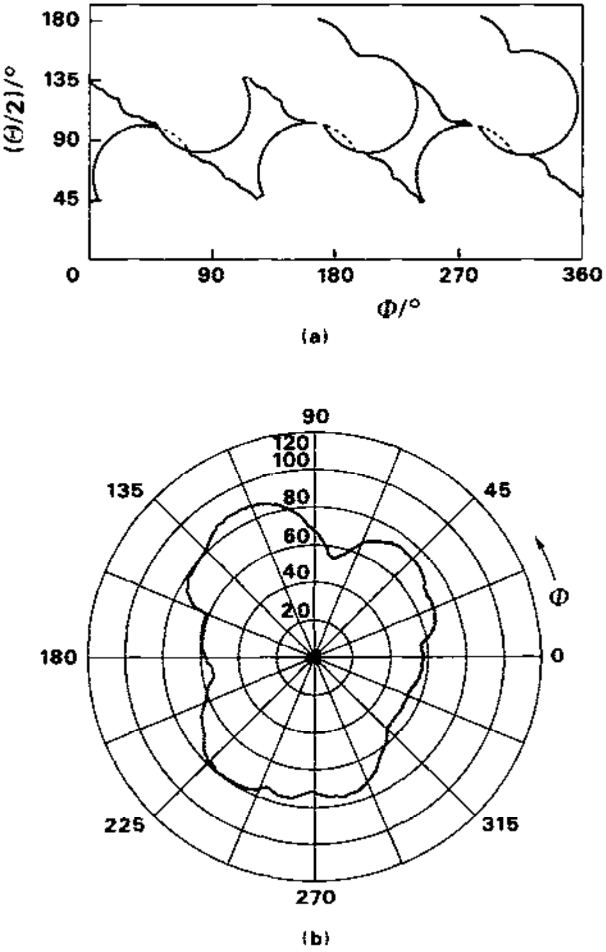


Fig. 3. The ligand profile in two graphic forms. (a) P(mesityl)$_3$ (adapted from ref. 57(b)); (b) PCy$_3$ (adapted from ref. 58).

atom of the ligand in a given orientation is defined. Then the ligand is allowed to rotate by an angle ϕ ($0 \leqslant \phi \leqslant 360°$) about the M—P bond and the $\theta/2$ angle corresponding to the new orientation is measured. A plot of $\theta/2$ as a function of ϕ gives the ligand profile. The two graphic forms illustrated in Fig. 3(a) and (b) have been adopted to represent the ligand profile of a number of phosphines [57,58].

3.1.4 *The solid angle factor*

The solid angle factor (SAF, Fig. 4) has been extensively used to analyse stereochemical demands of ligands (mostly other than phosphines or phosphites) in lanthanide and actinide complexes [59,60].

The solid angle factor is obtained by projecting a ligand towards a sphere of unit radii centred on the metal [59,60]. The numerical values of SAF are calculated from the corresponding solid angles Ω using eqn. (6). The solid angle factor represents the fraction of the sphere covered by a given ligand (θ is the Tolman cone angle). Using the SAF concept, it is possible to show in graphical form the non-circular boundary of a ligand and the existence of ligand intermeshing.

$$\mathrm{SAF} = \frac{\Omega}{4\pi} = \frac{1}{2}[1 - \cos(\theta/2)] \tag{6}$$

3.2 *Electronic properties of phosphorus(III) ligands*

The properties of phosphorus(III) ligands most extensively used to measure their σ donor/π acceptor characteristics are the pK_a and the carbonyl stretching frequency, ν_{CO}, in transition metal complexes containing phosphines and phosphites.

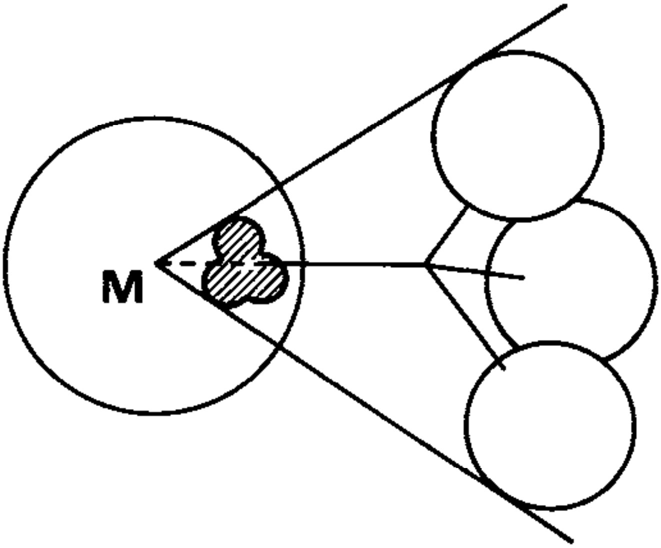


Fig. 4. The solid angle factor.

TABLE 3

Aqueous pK_a values, gas-phase proton affinities, and ionization energies of phosphorus(III) ligands

Molecule[a]	pK_a[b]	PA[c] (kJ mol^{-1})	IE[d] (eV)
PR_3			
PH_3	−14	789	9.869 ± 0.002
PF_3		697	11.44
PCl_3			9.91
PBr_3			9.7
PMe_3	8.65	950	8.06 ± 0.05
PEt_3	8.69	969	8.15 ± 0.11
$P(CH_2CH_2CN)_3$	1.37		
$P(CH_2CH_2Ph)_3$	6.60		
$P(CH_2CH_2OBu)_3$	8.03		
PPr_3	8.64		
PBu_3	8.43		(7.5)
$P(i\text{-}Bu)_3$	7.97		
$P(t\text{-}Bu)_3$	11.40		
$P(Pe)_3$	8.33		
PCy_3	9.70 9.65[e]		
PPh_3	2.73 2.73[e]	962	7.39 ± 0.03
$P(p\text{-}C_6H_4F)_3$	1.97[e]		
$P(m\text{-}C_6H_4Cl)_3$	(1.03)[f]		
$P(p\text{-}C_6H_4Cl)_3$	1.03[e]		
$P(o\text{-}Tol)_3$	3.08[e]		
$P(m\text{-}Tol)_3$	3.30[e]		
$P(p\text{-}Tol)_3$	3.84[e]		
$P(p\text{-}C_6H_4OMe)_3$	4.46 4.57[e]		
$P(p\text{-}C_6H_4NMe_2)_3$	8.65[e]		
PBz_3	(6.0)[f]		
$P(OMe)_3$	2.60[f]	923	(8.5)
$P(OEt)_3$	3.31[f]		(8.4)
$P(O\text{–}i\text{-}Pr)_3$	4.08[f]		
$P(OBu)_3$	(3.31)[f]		
$P(O\text{–}t\text{-}Bu)_3$	(4.5)[f]		
$P(OPh)_3$	−2.0[f]		
$P(O\text{–}o\text{-}Tol)_3$	−1.83[f]		
$P(O\text{–}o\text{-}C_6H_4\text{–}i\text{-}Pr)_3$	(−1.7)[f]		
$P(O\text{–}o\text{-}C_6H_4Ph)_3$	(−2.0)[f]		
$P(O\text{–}o\text{-}C_6H_4\text{–}t\text{-}Bu)_3$	(−1.0)[f]		
$P(O\text{–}2,6\text{-}C_6H_3Me_2)_3$	(−0.4)[f]		
$P(OMen)_3$	(3.7)[f]		
$P(NMe_2)_3$		924	6.75

TABLE 3 (*continued*)

Molecule[a]	pK_a[b]	PA[c] (kJ mol^{-1})	IE[d] (eV)
$P(NEt_2)_3$			⩽7.19
$P(NPr_2)_3$			⩽7.05
PRR'₂			
$PHMe_2$	3.91	905	8.47 ± 0.07
$PHEt_2$			(8.69)
$PH(CH_2CH_2CN)_2$	0.41 (−0.6)[f]		
$PH(CH_2CH_2Ph)_2$	3.46		
$PH(CH_2CH_2OBu)_2$	4.15		
$PHBu_2$	4.51		
$PH(i\text{-}Bu)_2$	4.11		
$PH(t\text{-}Bu)_2$			(7.9)
$PHCy_2$	4.55		
$PH(Oc)_2$	4.41		
$PFMe_2$			(8.8)
$PF(t\text{-}Bu)_2$			(8.2)
$PClMe_2$			(8.7)
$PCl(t\text{-}Bu)_2$			(8.0)
$PCl(NMe_2)_2$			(7.6)
$PMeH_2$		854	9.12 ± 0.07
$PMeF_2$			(9.8)
$PMeCl_2$			(9.5)
$PMeEt_2$	8.61		
$PMe(CH_2CH_2CN)_2$	3.61		
$PEtCl_2$			9.3
$PEtMe_2$	8.61		
$PEt(CH_2CH_2CN)_2$	3.80		
$P(CH_2CH_2CN)Me_2$	6.37		
$P(CH_2CH_2CN)(CH_2CH_2Ph)_2$	3.43		
$P(CH_2CH_2CN)Bu_2$	6.48		
$P(CH_2CH_2CN)[2,4\text{-}Pn(Me)_2]_2$	6.81		
$P(CH_2CH_2CN)Cy_2$	7.13		
$P(CH_2CH_2CN)Oc_2$	6.29		
$PBuH_2$	−0.03		
$P(i\text{-}Bu)H_2$	−0.02		
$P(t\text{-}Bu)H_2$			(8.9)
$P(t\text{-}Bu)F_2$			(9.2)
$P(t\text{-}Bu)Cl_2$			(9.0)
$P(C{\equiv}CCMe_3)H_2$			⩽9.05
$P(C{\equiv}CCMe_3)Cl_2$			⩽9.58
$PCyH_2$		880	
$P(Oc)H_2$	0.43		
$P(NMe_2)Cl_2$			(8.9)
$P(NMe_2)(OMe)_2$			(8.1)

TABLE 3 (*continued*)

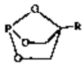
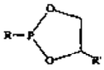
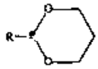
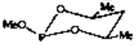
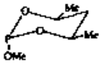
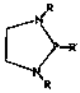
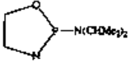
Molecule[a]	pK_a[b]	PA[c] (kJ mol^{-1})	IE[d] (eV)
PPh_2R			
PPh_2H	0.03		(7.80 ± 0.01)
PPh_2Me	4.57[f]	964	≤8.28 ± 0.05
PPh_2Et	4.9[f]		
$PPh_2(CH_2CH_2CN)$	2.27		
PPh_2(i-Pr)	(5.0)[f]		
PPh_2Cy	(5.05)[f]		
$PPh_2(OMe)$	(2.69)[f]		
$PPh_2(OEt)$	(2.91)[f]		
$PPh_2(OPh)$	(1.15)[f]		
$PPhR_2$			
$PPhH_2$	(−2.0)[f]	869	(8.47 ± 0.01)
$PPhMe_2$	6.50	961	7.58 ± 0.05
$PPhEt_2$	6.25		
$PPh(CH_2CH_2CN)_2$	3.20		
$PPh(OMe)_2$	(2.64)[f]		
$PPh(OEt)_2$	(3.1)[f]		(8.2)
$PPh(OPh)_2$	(−0.4)[f]		
$PPh(OMen)_2$	(4.2)[f]		
Other			
$PH(C_2H_4)$		801	(9.4 ± 0.1)
POCl			(11.5)
PN			11.85
 1		822	9.02[g]
 2			≤8.05 ± 0.10
 3			
R = H		812	
R = Me		829	
$P(OCH_2)_3CH$		867	(9.42 ± 0.10)
$P(OCH_2)_3CMe$		879	(9.2)
$P(OCH_2)_3CEt$	1.74[f]		

TABLE 3 (*continued*)

Molecule[a]	pK_a[b]	PA[c] (kJ mol^{-1})	IE[d] (eV)
 4		894	
 5			
R = OMe, R′ = H		890	(9.06 ± 0.10)
R = N(CHMe$_2$)$_2$, R′ = H			≤8.52
R = OMe, R′ = Me			(8.7)
 6			
R = OMe		918	(8.74 ± 0.10)
R = NMe$_2$			7.8
 7		941	(8.69 ± 0.10)
 8		946	(8.34 ± 0.10)
 9			(9.5)
 10			
R = Me, R′ = NMe$_2$			7.1
R = H, R′ = N(CHMe$_2$)$_2$			7.40
 11			≤7.74
P_2H_4			8.8 ± 0.1
P_2F_4			≤9.28
P[1,4-$C_6H_4(PH_2)_2$]H_2			≤8.78
PCl(*t*-Bu)(*t*-BuNH)			≤8.75

---

[a] Am = amyl; Bz = benzyl; Cy = cyclohexyl; Hex = hexyl; Men = menthyl; Oc = Octyl; Pe = pentyl; Tol = tolyl; 2,4-Pn(Me)$_2$ = 2,4-Dimethylpentyl.

[b] Values in parentheses are estimated. Data from ref. 61 unless indicated otherwise.

[c] Values in parentheses are estimated. Data from ref. 65.

[d] Values in parentheses are estimated. Data from ref. 65(a) unless indicated otherwise.

[e] Ref. 43.

[f] Ref. 44.

[g] Ref. 66.

It is usually assumed that ν_{CO} reflects both the σ electron donor and π acceptor ability, while pK_a is a measure of σ donicity alone. The analysis of the electronic properties of phosphines and phosphites in terms of ν_{CO}, pK_a, and some other important properties such as the proton affinity (PA) and the adiabatic ionization energy (IE), is made in this section.

3.2.1. The pK$_a$ values in aqueous solution, gas-phase proton affinities, and ionization energies

Table 3 includes a selection of experimental and estimated aqueous pK_a values of phosphorus(III) compounds reported in the literature [43,44,61]. Reliable estimates can usually be obtained by using methods based on the Hammett equation [61(b),62–64] when experimental data are not available.

The pK_a values of phosphorus(III) compounds have often been regarded as measuring their σ donation ability [19,41–44] because only a σ interaction is present when a phosphine or a phosphite binds to a proton. The aqueous pK_a, however, is not an absolute measure of the interaction between the proton and the phosphorus ligand since it is strongly affected by solvation effects. The importance of solvation in determining the pK_a can be evidenced by comparing the pK_a values in Table 3 with the corresponding proton affinities [65]. The pK_a is related to the change in Gibbs energy of the reaction

$$HPR_3^+(aq) \xrightarrow{\Delta G_a} H^+(aq) + PR_3(aq) \tag{7}$$

($\Delta G_a = 2.303RT\ pK_a$) and the proton affinity of PR_3 is the enthalpy change of the same reaction in the gas phase (reaction (8)). The relation between both quantities can be derived from Scheme 1, where ΔH_{d1}, ΔH_{d2}, and ΔH_{d3} are solvation enthalpies, and is given by eqns. (9) and (10). The data in Table 3 show that the gas-phase proton affinities do not always follow the same trends as the pK_a values. For example, the sequence $PMe_3 < PPhMe_2 < PPh_3 < PPh_2Me$ is observed for the proton affinities but the corresponding pK_a values are ordered according to $PMe_3 = PPhMe_2 = PPh_2Me = PPh_3$. The trend observed for the proton affinities is also followed by the adiabatic ionization energies (IE) of the above phosphines in the gas phase [65(a),66] (Table 3), which are related to the "availability" of the phosphorus lone pair of electrons to form the σ bond.

$$HPR_3^+(g) \xrightarrow{PA} H^+(g) + PR_3(g) \tag{8}$$

$$\begin{tikzcd}
HPR_3^+(aq) \arrow[r, "\Delta H_a"] & H^+(aq) + PR_3(aq) \\
HPR_3^+(g) \arrow[u, "\Delta H_{d1}"'] \arrow[r, "PA"] & H^+(g) + PR_3(g) \arrow[u, "\Delta H_{d2}", shift right=6] \arrow[u, "\Delta H_{d3}"', shift left=6]
\end{tikzcd}$$

Scheme 1.

$$pK_a = \frac{1}{2.303}\left(\frac{\Delta H_a}{RT} - \frac{\Delta S_a}{R}\right) \tag{9}$$

$$pK_a = \frac{PA}{2.303RT} - \frac{\Delta H_{d1} - \Delta H_{d2} - \Delta H_{d3}}{2.303RT} + \frac{\Delta S_a}{2.303R} \tag{10}$$

The proton affinity is a gas-phase value that corresponds to the enthalpy associated with the cleavage of the $H^+{-}PR_3$ bond. Therefore, if the Brønsted basicity (tendency to accept protons) of a phosphorus(III) ligand is to be used as a measure of its σ donation ability, it seems preferable to quote the PA instead of the pK_a. The ionization energy is related to the Lewis basicity (tendency to donate an electron pair) and is also a gas-phase value. The similar trends observed for IE and PA suggest that, in the gas phase, the Brønsted and Lewis basicities of phosphorus(III) compounds are probably equivalent (Fig. 5).

It has been pointed out that the use of the Brønsted basicity as a measure of the σ donation interaction in a metal–phosphorus bond may not be appropriate, since a proton is a hard acid and transition metals in low oxidation states that readily form complexes with phosphines and phosphites are much softer acids [44(c)]. Another objection that has been raised is the fact that, in the case of transition metals, the presence of M → P π back donation may affect the P → M σ donation due to the synergic nature of the M–P bond. While these questions are still unanswered, the basicity of phosphorus(III) compounds has proven to be an important concept to rationalize the structural and reactional trends in their chemistry with transition metals [1,2]. In particular, since most reactions are studied in solution,

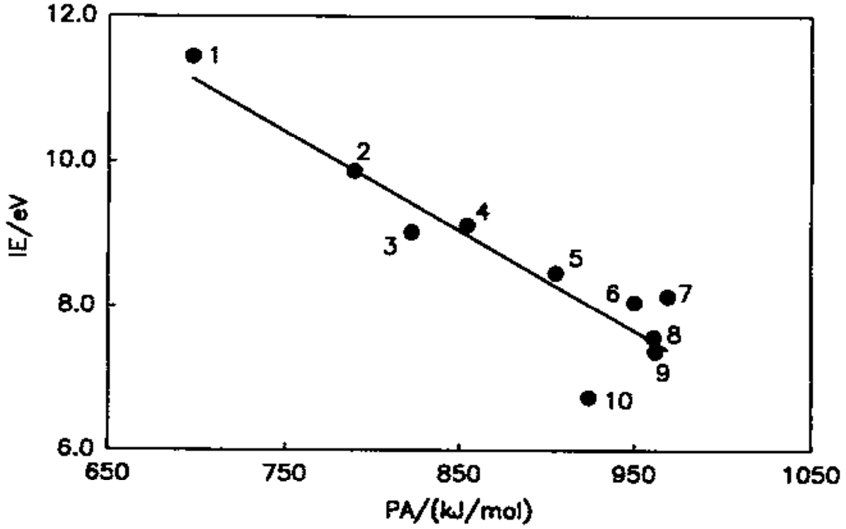


Fig. 5. Ionization energy as a function of the proton affinity of phosphorus(III) compounds. 1 = PF_3; 2 = PH_3; 3 = 3 (see Table 5); 4 = $PMeH_2$; 5 = $PHMe_2$; 6 = PMe_3; 7 = PEt_3; 8 = $PPhMe_2$; 9 = PPh_3; 10 = $P(NMe_2)_3$.

the pK_a values of phosphines and phosphites have been of great practical relevance in interpreting reactivity patterns and defining strategies of synthesis [1,2].

3.2.2. *The C–O stretching frequency*

For a given family of transition metal carbonyl complexes containing phosphorus(III) ligands, the A_1 CO stretching frequency increases as the electronegativity of the substituents on the phosphorus atom increases [8]. For example, in $Ni(CO)_3PR_3$ complexes, the following variation of ν_{CO} with R was observed [23,46(b)]: $R = Me < Ph < OMe < Cl < F$. The origin of this trend was initially attributed to the π acceptor properties of the PR_3 ligands [67]. Increasing the electronegativity of the R substituents increases the π acceptor ability of the PR_3 ligand and decreases the electron density on the metal available for $M \rightarrow CO$ back-donation. This results in a depopulation of the CO π^* orbital and in the strengthening of the C–O bond, which is reflected by the increase of ν_{CO}. More recently, however, results of DVM–HFS theoretical calculations suggested that the depopulation of the CO π^* orbital depends essentially on the σ donation ability of the phosphorus ligand [3]. This view is shared by other authors [19] based on the linear decrease of ν_{CO} as a function of the pK_a of PR_3 for a number of families of transition metal carbonyls. It seems likely that both the π acceptor and the σ donor abilities of PR_3 are reflected by the CO stretching frequency, but this subject is still a matter of controversy [3,19,32,44(c)].

Several scales of electron donor–acceptor properties of phosphorus(III) ligands have been proposed, based on the observed trends of the CO stretching frequencies in families of transition metal carbonyls [20–25,46(b)]. In particular, the scale proposed by Tolman [23,46(b)] has been widely used to explain and predict the reactivities of phosphines and phosphites in transition metal chemistry. Tolman examined the A_1 CO stretching frequencies of a considerable number of $Ni(CO)_3(PR_1R_2R_3)$ complexes dissolved in dichloromethane, and ordered the $PR_1R_2R_3$ ligands according to the assumption that the stronger their net donation ability the lower the corresponding CO frequency. He also found that the stepwise replacement of a substituent R_i by R_j in a $P(R_i)_3$ phosphine or phosphite changed ν_{CO} by a nearly constant increment [23,46(b)]. This led him to propose the equation

$$\nu_{CO}(\mathrm{cm}^{-1}) = 2056.1 + \sum_{i=1}^{3} \chi_i(\mathrm{cm}^{-1}) \tag{11}$$

to estimate ν_{CO} in these complexes, where χ_i represents the contribution of each substituent R_i, and $2056.1\ \mathrm{cm}^{-1}$ is the frequency corresponding to $P(t\text{-}Bu)_3$, the most basic ligand in the series (see Table 3), for which $\chi = 0$ ($\chi = \Sigma\chi_i$). The χ_i values for a variety of ligands are given in Table 4.

Bartik et al. [25] re-evaluated and extended Tolman's ν_{CO} data bank by using more accurate (FT–IR) measurements and derived a new set of χ_i values which are also included in Table 4. These authors showed that the additivity rule expressed by

TABLE 4

Substituent contribution, χ_i, to ν_{CO} in $Ni(CO)_3PR_1R_2R_3$ complexes

R[a]	χ_i[b] (cm^{-1})	R[a]	χ_i[b] (cm^{-1})
H	8.3[c]	2,4-$C_6H_3Me_2$	9.0[c]
F	18.2[c]	mesityl	2.7[c]
Cl	14.8[c]	CH_2-mesityl	2.48
CF_3	19.6[c]	1-naphthyl	3.93
Me	2.85, 2.6[c]	OMe	8.03, 7.7[c]
$CH{=}CH_2$	4.5[c]	OEt	7.20, 6.8[c]
Et	2.10, 1.8[c]	OCH_2CCl_3	11.9[c]
CH_2CH_2Cl	6.1[c]	OCH_2CHCH_2	7.7[c]
CH_2CH_2CN	7.45, 7.3[c]	OCH_2CH_2Cl	9.3[c]
C_3H_5	3.50	OCH_2CH_2CN	10.5[c]
Pr	1.80	OCH_2CH_2OMe	7.7[c]
i-Pr	1.15, 1.0[c]	OPr	6.97
Bu	1.75, 1.4[c]	O–i-Pr	6.35, 6.3[c]
i-Bu	1.90, 1.2[c]	OBu	6.95, 6.5[c]
s-Bu	1.72	O(*t*-Bu)	4.32
t-Bu	0.0	O(cyclopentyl)	6.17
Hex	1.67	OCy	6.00
Cy	0.47, 0.1[c]	$O(C_{18}H_{37})$	6.88
Oc	1.67	OPh	10.07, 9.7[c]
$C_{12}H_{25}$	1.67	O–*o*-C_6H_4Cl	11.4[c]
Ph	4.42, 4.3[c]	O–*p*-C_6H_4Cl	11.03
C_6F_5	11.2[c]	O–*p*-C_6H_4CN	12.62, 12.2
m-C_6H_4F	6.0[c]	O–*o*-Tol	9.68, 9.3[c]
p-C_6H_4F	5.23, 5.0[c]	O–*p*-Tol	9.3[c]
m-C_6H_4Cl	6.13	O–*p*-C_6H_4OMe	9.3[c]
p-C_6H_4Cl	5.60, 5.6[c]	O–*o*-C_6H_4-i-Pr	9.5[c]
o-Tol	3.55, 3.5[c]	O–*o*-C_6H_4-*t*-Bu	10.17, 9.6[c]
m-Tol	3.7[c]	O–*p*-C_6H_4-nonyl	9.45
p-Tol	3.5[c]	O–*o*-C_6H_4Ph	9.72
o-C_6H_4OMe	0.57, 0.9[c]	O(2-Me-4-Cl-C_6H_3)	10.67, 11.1[c]
p-C_6H_4OMe	3.50, 3.4[c]	OMen	5.62
p-$C_6H_4NMe_2$	1.75	O(bornyl)	5.77
Bz	3.45, 3.5[c]	OSPh	8.12
NMe_2	1.98, 1.9[c]	morpholino	3.73
N(i-Pr)$_2$	1.03	$SiMe_3$	0.27
piperidyl	2.0[c]		

[a] Bz = benzyl; Cy = cyclohexyl; Hex = hexyl; Oc = Octyl; Pe = pentyl; Tol = tolyl; Men = menthyl.

[b] Data from ref. 25 unless stated otherwise.

[c] Refs. 23 and 46(b).

eqn. (11) can lead to errors in ν_{CO} up to ca. 1 cm^{-1}, enough to change the order of some ligands in the scale of electron donor–acceptor properties. They proposed a scale of electron donor–acceptor properties of phosphorus(III) ligands, equivalent to Tolman's ν_{CO} scale, in terms of the difference, $^{FT}\chi$, between the observed CO stretching frequency corresponding to a given phosphorus(III) ligand and the frequency corresponding to P(t-Bu)$_3$ (eqn. (12)). The $^{FT}\chi$ values are given in Table 5.

$$\nu_{CO}(cm^{-1}) = 2056.1 + {}^{FT}\chi(cm^{-1}) \qquad (12)$$

4. THERMOCHEMISTRY OF TRANSITION METAL–PHOSPHORUS BONDS

Although the thermochemical data for complexes containing transition metal–phosphorus(III) ligands are not abundant, their correlation with other properties discussed in the previous sections may help understanding the systematics of metal–phosphine and metal–phosphite bond enthalpies, and lead to the prediction of new values. This is one of the goals of the present section, but it must be preceded by a critical analysis of the available thermochemical data, including a selection of the "best" values for the standard enthalpies of formation of the phosphorus(III) ligands. The effect of the nature of the phosphine or phosphite on the energetics of other metal–ligand bonds is not covered in this review. An example involving this important issue is, however, given at the end of this section.

4.1 *Thermochemical data of phosphorus(III) ligands*

The enthalpies of formation of phosphorus(III) ligands are collected in Table 6. Also included are data for oxides, because they may be useful in estimating enthalpies of formation of related phosphines and phosphites (see below). All values in Table 6 were recalculated from the original papers [68–106] and the auxiliary data used are listed in the Appendix. This task was greatly facilitated by the existence of several reviews [107–112].

Table 6 contains not only the selected standard enthalpies of formation, vaporization, and sublimation, but also indications of the experimental techniques used in the measurements. These are described by codes based in the classification by Cox and Pilcher [109]. Almost all vaporization and sublimation enthalpies listed were derived from vapour pressure–temperature data and, in these cases, it was often impossible to trace the experimental technique used by the authors. The only direct calorimetric measurement found is for $OPCl_3$. Whenever possible and/or necessary, the values of ΔH^0_v were corrected to 298.15 K. In the absence of experimental heat capacity data, which happened in most cases, the following estimate was used: $\Delta C_p(l \rightarrow g) = -54$ J mol^{-1} K^{-1} (Sidgwick's rule) [109]. The error of this estimate was not included in the uncertainty interval of ΔH^0_v. The values of ΔH^0_s were not corrected to 298.15 K. Enthalpies of vaporization/sublimation and uncertainty in-

TABLE 5

Electronic parameters $^{FT}\chi$ for phosphorus(III) ligands[a]

Molecule[b]	$^{FT}\chi$ (cm^{-1})	Molecule[b]	$^{FT}\chi$ (cm^{-1})
PR_3		$\text{P(O–}p\text{-C}_6\text{H}_4\text{-nonyl)}_3$	28.35
		$\text{P(O–}o\text{-C}_6\text{H}_4\text{Ph)}_3$	29.15
PCl_3	48.00	$\text{P[O(2-Me-4-Cl-C}_6\text{H}_3\text{)]}_3$	32.00
PMe_3	8.55	P(OMen)_3	16.85
PEt_3	6.30	P(Obornyl)_3	17.30
$\text{P(CH}_2\text{CH}_2\text{CN)}_3$	22.35	$\text{P(NMe}_2\text{)}_3$	5.95
$\text{P(C}_3\text{H}_5\text{)}_3$	10.50	$\text{P[N(i-Pr)}_2\text{]}_3$	3.10
PPr_3	5.40	P(morpholino)_3	11.20
P(i-Pr)_3	3.45	P(SPh)_3	24.35
PBu_3	5.25	$\text{P(SiMe}_3\text{)}_3$	0.80
P(i-Bu)_3	5.70		
$\text{P(}s\text{-Bu)}_3$	5.15	PRR'_2	
$\text{P(}t\text{-Bu)}_3$	0.00		
PHex_3	5.00	PHCy_2	9.10
PCy_3	1.40	$\text{PCl(}t\text{-Bu)}_2$	16.05
POc_3	5.00	$\text{PCl(}m\text{-C}_6\text{H}_4\text{F)}_2$	27.95
$\text{P(C}_{12}\text{H}_{25}\text{)}_3$	5.00	PMeCl_2	36.35
PPh_3	13.25	PMeCy_2	4.00
$\text{P(}p\text{-C}_6\text{H}_4\text{F)}_3$	15.70	PMeMen_2	2.40
$\text{P(}m\text{-C}_6\text{H}_4\text{Cl)}_3$	18.40	PMe(OMen)_2	14.60
$\text{P(}p\text{-C}_6\text{H}_4\text{Cl)}_3$	16.80	$\text{PMe(NMe}_2\text{)}_2$	6.10
$\text{P(}o\text{-Tol)}_3$	10.65	$\text{P(CH}_2\text{CH}_2\text{CN)H}_2$	23.05
$\text{P(}o\text{-C}_6\text{H}_4\text{OMe)}_3$	1.70	$\text{P(C}_3\text{H}_5\text{)Cy}_2$	4.75
$\text{P(}p\text{-C}_6\text{H}_4\text{OMe)}_3$	10.50	$\text{P(i-Pr)(}t\text{-Bu)}_2$	1.10
$\text{P(}p\text{-C}_6\text{H}_4\text{NMe}_2\text{)}_3$	5.25	P(i-Pr)Men_2	1.10
PBz_3	10.35	$\text{P(}t\text{-Bu)Cl}_2$	32.90
$\text{P(CH}_2\text{-mesityl)}_3$	7.45	$\text{P(}t\text{-Bu)(i-Pr)}_2$	2.55
P(1-naphthyl)_3	11.80	$\text{P(}t\text{-Bu)Cy}_2$	1.60
P(OMe)_3	24.10	$\text{P(}t\text{-Bu)Men}_2$	0.03
P(OEt)_3	21.60	$\text{P(}neo\text{-Pe)(}t\text{-Bu)}_2$	2.65
P(OPr)_3	20.90	$\text{P(}neo\text{-Pe)Men}_2$	2.20
P(O–i-Pr)_3	19.05	PCyH_2	16.75
P(OBu)_3	20.85	$\text{PCy(}m\text{-C}_6\text{H}_4\text{OMe)}_2$	5.20
$\text{P(O–}t\text{-Bu)}_3$	12.95	PCyMen_2	0.45
$\text{P(O–cyclopentyl)}_3$	18.50	$\text{P(CH}_2\text{Cy)Men}_2$	1.50
P(OCy)_3	18.00	PBzMen_2	3.60
$\text{P(OC}_{18}\text{H}_{37}\text{)}_3$	20.65	PBz(OMen)_2	15.15
P(OPh)_3	30.20	PMenCl_2	32.20
$\text{P(O–}p\text{-C}_6\text{H}_4\text{Cl)}_3$	33.10	PMenMe_2	5.30
$\text{P(O–}p\text{-C}_6\text{H}_4\text{CN)}_3$	37.85	PMen(OMe)_2	15.60
$\text{P(O–}o\text{-Tol)}_3$	29.05	PMen(OEt)_2	14.05
$\text{P(O–}o\text{-C}_6\text{H}_4\text{-}t\text{-Bu)}_3$	30.50	$\text{P(1-naphthyl)Men}_2$	4.35

TABLE 5 (*continued*)

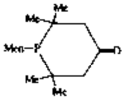
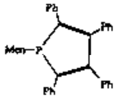
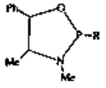
Molecule[b]	$^{FT}\chi$ (cm^{-1})
PPh_2R	
PPh_2H	17.35
PPh_2Cl	24.65
PPh_2Me	12.10
$PPh_2(CH{=}CH_2)$	13.65
PPh_2Et	11.30
$PPh_2(C_3H_5)$	12.40
PPh_2Pr	11.15
PPh_2(i-Pr)	10.85
PPh_2Bu	11.10
PPh_2(*t*-Bu)	8.95
PPh_2Pe	11.00
PPh_2Hex	10.90
$PPh_2(p\text{-}C_6H_4Br)$	14.45
PPh_2(*o*-Tol)	12.75
PPh_2(*p*-Tol)	11.90
$PPh_2(o\text{-}C_6H_4OMe)$	10.30
$PPh_2(o\text{-}C_6H_4SMe)$	11.40
$PPh_2(o\text{-}C_6H_4Ph)$	11.95
PPh_2Bz	12.30
PPh_2Men	10.25
PPh_2(*neo*-Men)	9.70
$PPh_2(OMe)$	16.30
$PPh_2(OEt)$	15.60
$PPh_2(OPr)$	15.45
$PPh_2(OBu)$	15.35
PPh_2(O—cyclopentyl)	14.85
$PPh_2(OCy)$	14.65
$PPh_2(OC_{18}H_{37})$	15.20
$PPh_2(OPh)$	18.95
$PPh_2(OMen)$	14.75
$PPh_2(NEt_2)$	10.90
$PPh_2[N(i\text{-}Pr)_2]$	10.65
$PPh_2(SPh)$	17.35
$PPh_2(SiMe_3)$	8.05
$PPhR_2$	
$PPhH_2$	20.85
$PPhCl_2$	36.40
$PPhMe_2$	10.60
$PPh(CH{=}CH_2)_2$	14.05
$PPhEt_2$	9.30
$PPh(C_3H_5)_2$	11.60
$PPhPr_2$	8.80
$PPh(i\text{-}Pr)_2$	7.50
$PPhBu_2$	8.60
$PPh(t\text{-}Bu)_2$	4.95
$PPhPe_2$	8.50
$PPhHex_2$	8.45
$PPhBz_2$	11.90
$PPh(o\text{-}Tol)_2$	11.90
$PPh(Men)_2$	4.25
$PPh(neo\text{-}Men)_2$	4.25
$PPh(OMe)_2$	19.45
$PPh(OEt)_2$	18.10
$PPh(OPr)_2$	17.70
$PPh(OBu)_2$	17.60
$PPh(O{-}t\text{-}Bu)_2$	13.15
$PPh(O\text{—cyclopentyl})_2$	16.25
$PPh(OCy)_2$	15.85
$PPh(OC_{18}H_{37})_2$	17.45
$PPh(OPh)_2$	24.10
$PPh(OMen)_2$	15.55
$PPh(NMe_2)_2$	9.50
$PPh(NEt_2)_2$	8.15
$PPh(SPh)_2$	21.45
$PPh(SiMe_3)_2$	4.25
Other	
$PPh({=}CHCH_3)$	13.15
PPhHMe	15.25
PPhBr(*t*-Bu)	12.90
PPh(i-Pr)(OMen)	12.10
PMe(i-Pr)Men	4.40
PMe(*t*-Bu)Men	3.55
PMeCyMen	3.65
$P(OCH_2)_3CMe$	31.80
$P(OCH_2)_3CEt$	31.20
 12	6.75

TABLE 5 (*continued*)

Molecule[b]	$^{FT}\chi$ (cm^{-1})	Molecule[b]	$^{FT}\chi$ (cm^{-1})
 13	10.60		
 14			
		R = Me	15.80
		R = *t*-Bu	11.05
		R = Ph	18.85

[a] Data from ref. 25.

[b] Bz = benzyl; Cy = cyclohexyl; Hex = hexyl; Oc = Octyl; Pe = pentyl; Tol = tolyl; Men = menthyl.

tervals estimated in the original papers are indicated in parentheses. When no indication of the error bars was stated by the authors, the estimate given by Cox and Pilcher [109] was adopted.

From the analysis of the data in Table 6, it can be concluded that the differences between the enthalpies of formation of phosphines, phosphites, and corresponding oxides, in their standard reference states (rs), i.e. their stable physical states at 298.15 K and 10^5 Pa, are approximately constant within families of compounds (X = halogen; R = alkyl or aryl):

$$\Delta H_f^0(\mathrm{PX_3, rs}) - \Delta H_f^0(\mathrm{OPX_3, rs}) = 289 \pm 3\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_f^0(\mathrm{PR_3, rs}) - \Delta H_f^0(\mathrm{OPR_3, rs}) = 341 \pm 7\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_f^0[\mathrm{P(OR)_3, rs}] - \Delta H_f^0[\mathrm{OP(OR)_3, rs}] = 359 \pm 15\ \mathrm{kJ\ mol^{-1}}$$

The same trend is also apparent in Figs. 6–8 where the reference state enthalpies of formation of PX_3, OPX_3, PR_3, OPR_3, $P(OR)_3$, and $OP(OR)_3$ are plotted against the reference state enthalpies of formation of the corresponding HX, RH, or ROH. This type of correlation has been applied to assess the thermochemical data of a variety of inorganic and organometallic compounds [113]. Its modest success for estimating accurate values of the enthalpies of formation of the above compounds may indicate internal inconsistencies of the data, although in some cases the number of values available is not enough to confirm this possibility. The value of the correlation itself can be questioned, as suggested by the following example. The linear regression involving the *n*-alkylphosphites (eqn. (13); $r = 0.992$), is considerably worse than a correlation where the enthalpies of formation are plotted against the

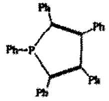
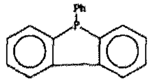
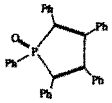
TABLE 6

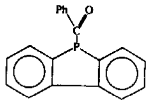
Standard enthalpies of formation of phosphines, phosphites and oxides
Data in kJ mol^{-1} [a,b]

Compound[c]	ΔH_f^0(l/c)	$\Delta H_v^0/\Delta H_s^0$	ΔH_f^0(g)
PR₃			
PH_3,g			5.4 ± 1.7 [ED/68]
PF_3,g			−957.7 ± 0.9 [FCC/69]
PCl_3,l	−318.9 ± 1.9 [RSC/70,71]	32.9 ± 0.5 [PT2/72–74]	−286.0 ± 2.0
PBr_3,l	−183.9 ± 2.8 [RSC/71]	43.3 ± (3.8) [PT2/75]	−140.6 ± 4.7
PI_3,c	−56.8 ± 2.0 [RSC/76(a)]	63.7 ± 8.0 [PT2/76(b)]	6.9 ± 8.2
$P(CN)_3$,c	407.9 ± 24.0 [RSC/77]	75.3 ± 6.0 [PT2/77(a)]	483.2 ± 24.7
PMe_3,l	−129.1 ± 4.8 [SB/78]	29.1 ± (2.1) [PT2/79]	−100.0 ± 5.2
PEt_3,l	−89.1 ± 11.8 [SB/80–82]	39.7 ± (2.1) [PT2/83]	−49.4 ± 12.0
	(−148)		(−108) [106]
$P(CH_2CH_2CN)_3$,c		105.7 ± 2.0 [PT1/84]	
PPr_3,l	[d][RSC/85]		
PBu_3,l	−122.8 ± 35.0 [RSC/85]		
$PHex_3$,l	−745.9 ± 39.2 [RSC/86]		
PPh_3,c	211.3 ± 3.5 [RB/87]	113.2 ± 3.0 [PT2/84,87–89]	324.5 ± 4.6
PPh_3,l	228.3 ± 3.5 [87]	96.2 ± 3.0 [M/87]	324.5 ± 4.6
P(*p*-Tol)$_3$,l		131.9 ± 5.0 [PT1/84]	
$P(OMe)_3$,l	−748.5 ± 15.5 [RSC/90]	36.8 ± (4.2) [PT3/90]	−711.7 ± 16.1
$P(OEt)_3$,l	−864.1 ± 11.0 [RSC/90,91]	41.8 ± (4.2) [PT3/91]	−822.3 ± 11.8
P(O-i-Pr)$_3$,l	−986.3 ± 15.2 [RSC/91]	46.0 ± (4.2) [PT3/91]	−940.3 ± 15.8
$P(OBu)_3$,l	−1104.4 ± 12.9 [RSC/86]		
$P(NEt_2)_3$,l	−286.2 ± 13.2 [RSC/93]	60.7 ± 0.4 [PT3/93]	−225.5 ± 13.2

PRR'_2			
$PCl(NEt_2)_2$,l	−332.4 ± 8.9 [RSC/96]		
$PEtCl_2$,l	−314.7 ± 20.4 [RSC/95]		
$P(NEt_2)Cl_2$,l	−346.2 ± 5.7 [RSC/96]		
OPR_3			
OPF_3,g			−1253.1 ± 8.6 [97]
$OPCl_3$,l	−606.4 ± 1.4 [RSC/70,71]	38.58 ± 0.01 [C/98]	−567.8 ± 1.4
$OPBr_3$,c	−468.6 ± 2.3 [RSC/71]		
$OPMe_3$,c	−484.6 ± 6.4 [RSC/99]	(50.2 ± 4.2) [99]	−434.4 ± 7.7
$OPPr_3$,c	^{d}[RSC/85]		
$OPBu_3$,c	−467.1 ± 32.6 [SB/100,101]		
$OPHex_3$,c	−1107.7 ± 44.0 [SB/86]		
$OPPh_3$,c	−112.1 ± 3.5 [RB/87]	131.0 ± 2.0 [PT1/102]	18.9 ± 4.0
$OP(OMe)_3$,l		53.3 ± 0.9 [PT2/92]	
$OP(OEt)_3$,l	−1253.6 ± 13.5 [RSC/85,103]	57.9 ± 0.7 [PT2/92]	−1195.7 ± 13.5
$OP(OPr)_3$,l	−1321.8 ± 22.1 [SB/100]	65.7 ± 1.1 [PT2/92]	−1256.1 ± 22.1
$OP(O\text{–}i\text{-}Pr)_3$,l	−1306.7 ± 15.7 [RSC/95]		
$OP(OBu)_3$,l	−1460.3 ± 11.4 [SB/100,101]	72.5 ± 4.5 [PT2/92]	−1387.8 ± 12.3
$OP(O\text{–}i\text{-}Bu)_3$,l	−1454.2 ± 31.7 [SB/101]	72.6 ± 0.7 [PT2/92]	−1381.6 ± 31.7
$OP(OPh)_3$,c	−753.7 ± 12.3 [SB/101]		
$OPRR'_2$			
$OP(H)Ph_2$,c	−520.9 ± 24.4 [SB/94]		
$OP(H)(OEt)_2$,l	^{e}[RSC/95]	29.3 ± (4.2) [PT3/95]	
$OP(OH)(OEt)_2$,l	^{e}[RSC/95] ^{f}[RSC/95]	41.8 ± (4.2) [PT3/95]	
$OPF(OEt)_2$,l	^{f}[RSC/95]	46.0 ± (4.2) [PT3/95]	
$OPMe(OH)_2$,c	−1056.1 ± 29.2 [RSC/95]	48.1 ± (4.2) [PT3/95]	−1008.0 ± 29.5
$OPMeCl_2$,c	−621.5 ± 29.2 [RSC/91]	62.3 ± (4.2) [PT3/91]	−559.2 ± 29.5

TABLE 6 (*continued*)

Compound^c	ΔH_f^0(l/c)	$\Delta H_v^0/\Delta H_s^0$	ΔH_f^0(g)
$OPMe(OEt)_2$,l	−1038.2 ± 29.4 [RSC/91]	56.5 ± (4.2) [PT3/91]	−981.7 ± 29.7
$OPMe(NHPh)_2$,c	−365.5 ± 25.1 [SB/91]		
$OPEt(OH)_2$,c	−1075.3 ± 19.5 [RSC/95,104]	50.6 ± (4.2) [PT3/95]	−1024.7 ± 19.9
$OPEtCl_2$,l	−630.6 ± 19.5 [RSC/91]	42.7 ± (4.2) [PT3/91]	−587.9 ± 19.9
$OPEt(O{-}i{-}Pr)_2$,l	−1144.8 ± 19.6 [RSC/91]	60.7 ± (4.2) [PT3/91]	−1084.1 ± 20.0
$OPEt(NHPh)_2$,c	−378.4 ± 12.6 [SB/91]		
$OPPh(OH)_2$,c	−890.5 ± 10.8 [SB/94]		
$OP(OBu)Bu_2$,l	−770.4 ± 47.1 [SB/100]		
Other			
OP(H)(OH)Ph,c	−559.0 ± 20.2 [SB,RSC/94]		
OP(O–i-Pr)(Me)OH,l	^{g}[RSC/95]	60.7 ± (4.2) [PT3/95]	
OP(O–i-Pr)(Me)Cl,l	^{g}[RSC/95]	58.6 ± (4.2) [PT3/95]	
 ,c 15	387.8 ± 14.3 [SB/105]		
 ,c 16	183.1 ± 8.5 [SB/105]		
 ,c 17	216.6 ± 21.8 [SB/105]		

 ,c 18	93.9 ± 25.1 [SB/105]

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[a] Values in parentheses are estimated.

[b] ED = explosive decomposition at constant volume in an isothermal calorimeter; FCC = fluorine combustion calorimetry; RB = rotating bomb combustion calorimetry; SB = static bomb combustion calorimetry; C = direct calorimetric measurement; RSC = reaction–solution calorimetry; M = result obtained using the enthalpy of fusion of the solid; PT1 = accurately measured P–T data fitted to a simplified Clark and Glew equation and, in the case of ΔH_v, corrected to 298.15 K; PT2 = measured P–T data fitted to Clausius–Clapeyron equation and, in the case of ΔH_v, corrected to 298.15 K if the average temperature is much different from 298.15 K; PT3 = data obtained from Clausius–Clapeyron plot with unstated temperature range and therefore not corrected to 298.15 K.

[c] Hex = hexyl; Tol = tolyl.

[d] $\Delta H_f^0[\mathrm{PPr_3,l}] - \Delta H_f^0[\mathrm{OPPr_3,c}] = 348.8 \pm 8.4\ \mathrm{kJ\ mol^{-1}}$.

[e] $\Delta H_f^0[\mathrm{OP(H)(OEt)_2,l}] - \Delta H_f^0[\mathrm{OP(OH)(OEt)_2,l}] = 349.4 \pm 3.5\ \mathrm{kJ\ mol^{-1}}$.

[f] $\Delta H_f^0[\mathrm{OPF(OEt)_2,l}] - \Delta H_f^0[\mathrm{OP(OH)(OEt)_2,l}] = -3.1 \pm 2.4\ \mathrm{kJ\ mol^{-1}}$.

[g] $\Delta H_f^0[\mathrm{OP(O{-}i{-}Pr)(Me)Cl,l}] - \Delta H_f^0[\mathrm{OP(O{-}i{-}Pr)(Me)OH,l}] = 219.3 \pm 2.6\ \mathrm{kJ\ mol^{-1}}$.

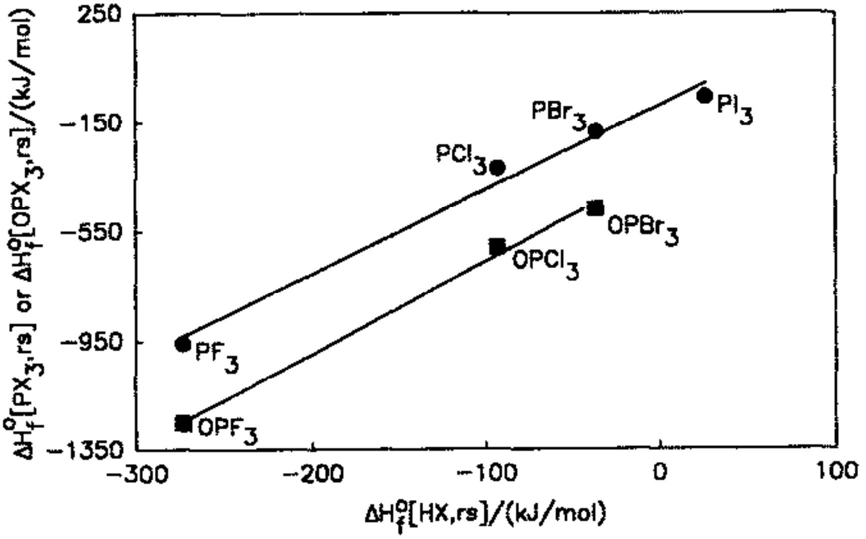


Fig. 6. Enthalpies of formation of phosphorus trihalides, PX_3, and phosphoryl halides, OPX_3, in their standard reference states as a function of the enthalpies of formation of gaseous HX.

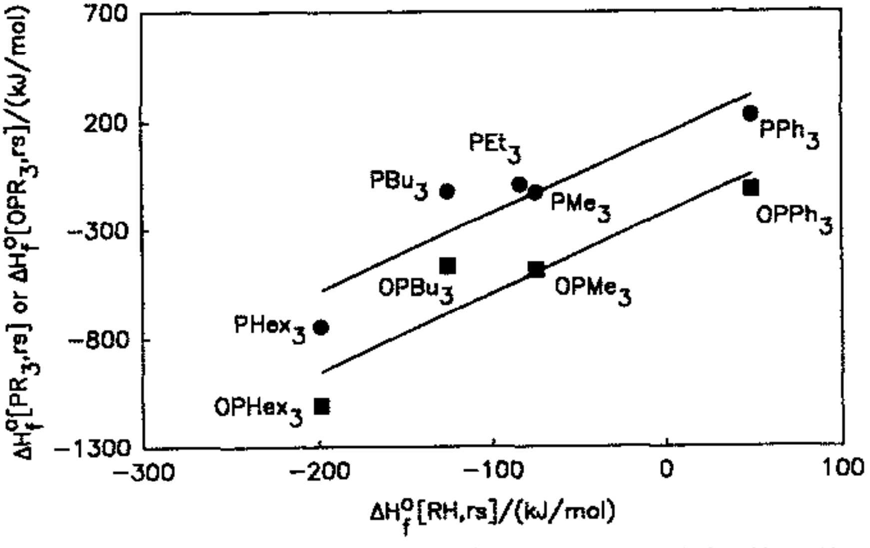


Fig. 7. Enthalpies of formation of alkyl and phenyl phosphines, PR_3, and phosphine oxides, OPR_3, in their standard reference states as a function of the standard reference state enthalpies of formation of RH.

molecular weight, *M*, (eqn. (14); $r = 0.99996$). Note, however, that the large error of the intercept in eqn. (13) is caused by a long extrapolation, since the enthalpies of formation of the alcohols used in the correlation are very negative. Figures 6–8 are nevertheless useful to ascertain what data are most likely to be wrong. For example,

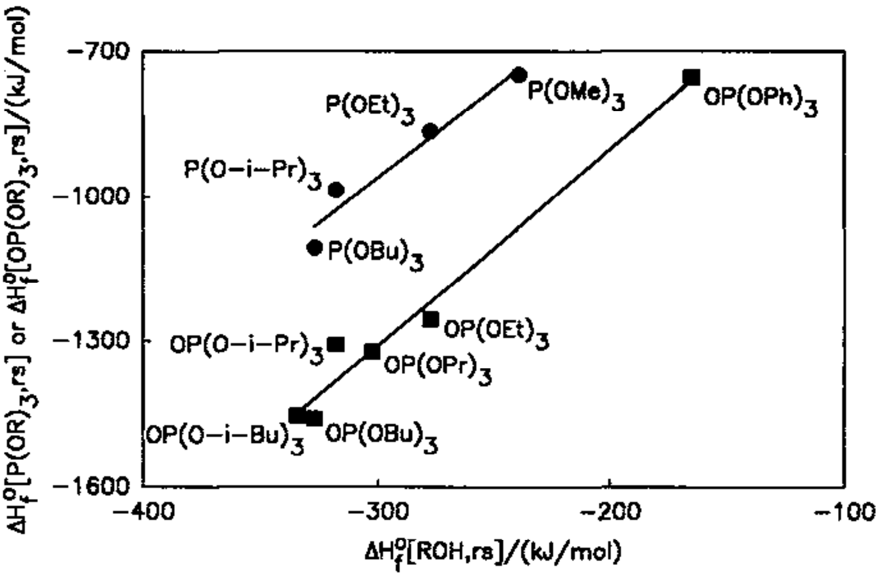


Fig. 8. Enthalpies of formation of alkyl phosphites, $P(OR)_3$, and alkyl and phenyl phosphite oxides, $OP(OR)_3$, in their standard reference states as a function of the standard reference state enthalpies of formation of ROH.

Fig. 7 suggests that some phosphines and/or phosphine oxides should be reinvestigated. This situation reflects the fact that many of the data were obtained by static bomb combustion calorimetry and this method may not be adequate for phosphorus compounds due to the difficulty in analysing the final state [111,114]. An example is given by PBu_3 and $OPBu_3$. The enthalpy of formation of $OPBu_3$ was determined using a static bomb combustion calorimeter and then used to derive $\Delta H_f^0(PBu_3, l)$ from reaction–solution calorimetric studies. The difference $\Delta H_f^0(PBu_3, l) - \Delta H_f^0(OPBu_3, c) = 344.3$ kJ mol^{-1} can be obtained from reaction–solution calorimetry alone and is in the range found for other phosphines (see above), suggesting that $\Delta H_f^0(OPBu_3, c)$ is probably in error. Contrasting with this situation, Fig. 8 suggests that the data for phosphites have fair internal consistency. All phosphites in Fig. 8 were studied by reaction–solution calorimetry, from reaction of PCl_3 with the appropriate alcohol, and the ΔH_f^0 values are all anchored in the combustion measurement for PCl_3.

$$\Delta H_f^0[P(OR)_3, rs] = (4.073 \pm 0.512)\Delta H_f^0(ROH, rs) + (240.2 \pm 145.3) \qquad (13)$$

$$\Delta H_f^0[P(OR)_3, rs] = (2.824 \pm 0.027)M - (396.7 \pm 5.0) \qquad (14)$$

Many of the enthalpies of vaporization/sublimation in Table 6 have an unstated temperature range and/or estimated uncertainty interval. Therefore, even for simple compounds such as PMe_3, ΔH_v^0 should be redetermined. It is generally observed that ΔH_v^0 or ΔH_s^0 correlate with the molecular weight within families of phosphorus

TABLE 7

Metal–phosphorus bond dissociation enthalpies
Data in kJ mol^{-1}

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
Lanthanides		
$[Sm(Cp^*)_2H]_2$(soln) + $2Et_2PH$(soln) = $2Sm(Cp^*)_2PEt_2$(soln) + $2H_2$(g) (RSC, toluene, 118)	−45.2 ± 3.4	136 ± 8[d]
Group 4		
$Ti(C_6H_9)_2PEt_3$(soln) = $Ti(C_6H_9)_2$(soln) + PEt_3(soln) (ES, thf, 49)	61.1 ± 2.9	61 ± 3
$Ti(C_7H_{11})_2L$(soln) = $Ti(C_7H_{11})_2$(soln) + L(soln) (ES, thf, 49)		
L = PMe_3	60.7 ± 3.3	61 ± 3
L = PEt_3	41.8 ± 0.4	42 ± 1
L = $PPhMe_2$	54.0 ± 2.1	54 ± 2
L = $P(OMe)_3$	47.7 ± 3.8	48 ± 4
L = $P(OEt)_3$	44.4 ± 2.5	44 ± 3
L = PF_3	72.8 ± 3.3	73 ± 3
Group 6		
$Cr(CO)_3(PCy_3)_2$(soln) + $P(OMe)_3$(soln) = $Cr(CO)_3(PCy_3)_2P(OMe)_3$(soln) (RSC, toluene, 128)	−68.6 ± 2.5	69 ± 3
$Cr(CO)_5L$(soln) + CO(soln) = $Cr(CO)_6$(soln) + L(soln) (KS, decane, 120)		
L = PPh_3	−16.3 ± 8.3	138 ± 15[e]
L = $P(OPh)_3$	−34.7 ± 5.2	119 ± 14[e]
$Cr(CO)_5$(heptane)(soln) + PBu_3(soln) = $Cr(CO)_5PBu_3$(soln) (PAC, heptane, 122)	−90.4 ± 5.0	131 ± 14[f]
$Mo(Cp)(CO)_3H$(soln) + L(soln) = $Mo(Cp)(CO)_2(L)H$ + CO(soln) (RSC, thf, 124)		
L = PMe_3	−22.6 ± 1.4	L1 + (23 ± 1)[g]
L = PBu_3	−20.9 ± 0.6	L1 + (21 ± 1)[g]
L = PPh_3	−5.0 ± 2.9	L1 + (5 ± 3)[g]
L = $PPhMe_2$	−15.9 ± 0.9	L1 + (16 ± 1)[g]
L = PPh_2Me	−6.7 ± 0.6	L1 + (7 ± 1)[g]
L = $P(OMe)_3$	−19.3 ± 0.6	L1 + (19 ± 1)[g]
$Mo(Cp)(CO)_3R$(soln) + L(soln) = $Mo(Cp)(CO)_2(L)C(O)R$(soln) (RSC, S, 124, 126)		
S = thf R = Me L = PMe_3	−82.4 ± 1.4	L2 + (82 ± 1)[h]
L = PBu_3	−77.8 ± 1.4	L2 + (78 ± 1)[h]
L = $PPhMe_2$	−71.6 ± 0.9	L2 + (72 ± 1)[h]
L = PPh_2Me	−59.4 ± 0.9	L2 + (59 ± 1)[h]
L = $P(OMe)_3$	−72.0 ± 0.6	L2 + (72 ± 1)[h]
R = Et L = PMe_3	−94.1 ± 1.4	L3 + (94 ± 1)[h]
L = PBu_3	−91.2 ± 0.6	L3 + (91 ± 1)[h]
L = PPh_3	−64.4 ± 1.7	L3 + (64 ± 2)[h]
L = $PPhMe_2$	−82.4 ± 0.6	L3 + (82 ± 1)[h]
L = PPh_2Me	−76.1 ± 0.6	L3 + (76 ± 1)[h]
L = $P(OMe)_3$	−82.8 ± 1.4	L3 + (83 ± 1)[h]

TABLE 7 (*continued*)

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
S = MeCN R = Bz L = PMe_3	−91.6 ± 2.1	L4 + (92 ± 2)[h]
L = PPh_3	−59.0 ± 5.0	L4 + (59 ± 5)[h]
L = $PPhMe_2$	−79.9 ± 1.7	L4 + (80 ± 2)[h]
L = PPh_2Me	−66.1 ± 2.1	L4 + (66 ± 2)[h]
L = $P(OMe)_3$	−73.2 ± 2.1	L4 + (73 ± 2)[h]
$[Mo(Cp)(CO)_2]_2$(soln) + 2L(soln) = $[Mo(Cp)(CO)_2L]_2$(soln) (RSC, thf, 126)		
L = PPh_2Me	−114.6 ± 2.5	
L = $P(OMe)_3$	−164.0 ± 8.4	
$[Mo(Cp)(CO)_3]_2$(soln) + 2L(soln) = $[Mo(Cp)(CO)_2L]_2$(soln) + 2CO(soln) (thf, 126)		
L = PPh_2Me	54.0 ± 2.9[i]	L5 − (27 ± 1)[i]
L = $P(OMe)_3$	4.6 ± 8.5[i]	L5 − (2 ± 4)[i]
$Mo(CO)_3(PCy_3)_2$(soln) + $P(OMe)_3$(soln) = $Mo(CO)_3(PCy_3)_2P(OMe)_3$(soln) (RSC, toluene, 128)	−100.4 ± 4.2	100 ± 4
$Mo(CO)_3(PhMe)$(soln) + 3L(soln) = $Mo(CO)_3L_3$(soln) + PhMe(soln) (RSC, thf, 123)		
L = PMe_3	−209.7 ± 0.4	156 ± 1[j]
L = PEt_3	−187.1 ± 1.7	148 ± 1[j]
L = PBu_3	−198.0 ± 0.8	152 ± 1[j]
L = $P(t\text{-}Bu)_3$	−41.1 ± 0.4[k]	< 149[l]
L = PPh_3	−168.2 ± 3.8	142 ± 1[j]
L = PCy_3	−88.3 ± 0.8[k]	< 173[l]
L = $PPhMe_2$	−195.9 ± 1.3	151 ± 1[j]
L = PPh_2Me	−168.2 ± 0.4	142 ± 1[j]
L = $P(OMe)_3$	−211.3 ± 2.1	156 ± 1[j]
L = $P(OPh)_3$	−169.5 ± 0.4	142 ± 1[j]
L = PCl_3	−105.9 ± 2.9	121 ± 1[j]
L = triphos	−184.1 ± 2.5	147 ± 1[j]
$Mo(CO)_6$(soln) + $2PPh_2Me$(soln) = $Mo(CO)_4(PPh_2Me)_2$(soln) + 2CO(soln) (RSC, dcdc, 124)	−6.7 ± 4.2	161 ± 4[m]
$Mo(CO)_4(nbd)$(soln) + 2L(soln) = *cis*-$Mo(CO)_4L_2$(soln) + nbd(soln) (RSC, thf, 125)		
L = PMe_3	−137.7 ± 0.4	179 ± 1[n]
L = PEt_3	−134.3 ± 0.4	178 ± 1[n]
L = PBu_3	−125.9 ± 0.4	174 ± 1[n]
L = PPh_3	−71.5 ± 0.4	146 ± 1[n]
L = $PPhMe_2$	−112.1 ± 1.7	167 ± 1[n]
L = PPh_2Me	−92.9 ± 0.8	157 ± 1[n]
L = $P(OMe)_3$	−115.1 ± 0.4	168 ± 1[n]
L = $P(OPh)_3$	−91.6 ± 0.4	156 ± 1[n]
L = PCl_3	−31.0 ± 0.8	126 ± 1[n]
$Mo(CO)_4(nbd)$(soln) + L(soln) = $Mo(CO)_4L$(soln) + nbd(soln) (RSC, thf, 125)		
L = $Me_2PCH_2PMe_2$	−102.5 ± 2.1	324 ± 2[o]
L = $(Me_2PCH_2)_2$	−135.6 ± 0.4	357 ± 1[o]
L = $Ph_2PCH_2PPh_2$	−66.9 ± 0.8	288 ± 1[o]
L = diphos	−101.7 ± 1.3	323 ± 1[o]
L = $Ph_2P(CH_2)_3PPh_2$	−96.2 ± 0.4	317 ± 1[o]
L = $Ph_2P(CH_2)_4PPh_2$	−92.5 ± 0.4	314 ± 1[o]
L = $o\text{-}C_6H_4(PPh_2)_2$	−103.3 ± 3.3	324 ± 3[o]
L = $Ph_2PCH_2CH_2AsPh_2$	−80.8 ± 0.4	302 ± 1[o]
L = $Ph_2AsCH_2CH_2AsPh_2$	−49.8 ± 1.3	271 ± 1[o]

TABLE 7 (*continued*)

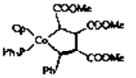
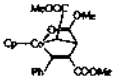
Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
$W(CO)_3(PCy_3)_2$(soln) + $P(OMe)_3$(soln) = $W(CO)_3(PCy_3)_2P(OMe)_3$(soln) (RSC, S, 127)		
S = toluene	−110.9 ± 6.3	111 ± 6
S = thf	−105.0 ± 5.4	105 ± 5
$W(CO)_3(PCy_3)_2(H_2)$(soln) + $P(OMe)_3$(soln) = $W(CO)_3(PCy_3)_2P(OMe)_3$(soln) + H_2(g) (RSC, S, 127)		
S = toluene	−67.8 ± 2.1	
S = thf	−65.3 ± 1.7	
$W(CO)_5(PhNH_2)$(soln) + L(soln) = $W(CO)_5L$(soln) + $PhNH_2$(soln) (ES, toluene, 132)		
L = PBu_3	31.8 ± 10.9	L6 − (32 ± 11)[p]
L = PPh_3	103.8 ± 6.7	L6 − (104 ± 7)[p]
L = $P(OBu)_3$	59.4 ± 7.5	L6 − (59 ± 8)[p]
L = $P(OPh)_3$	109.6 ± 2.1	L6 − (110 ± 2)[p]
Group 8		
$Fe(Cp)(C_6H_6)^+$(soln) + $3P(OMe)_3$(soln) = $Fe(Cp)[P(OMe)_3]_3^+$(soln) + C_6H_6(soln) (EC, MeCN/0.1 M $Bu_4N^+BF_4^-$, 133)	−202 ± 5	
$Ru(Cp^*)(PMe_3)_2X$(soln) = $Ru(Cp^*)(PMe_3)X$(soln) + PMe_3(soln) (KS, *o*-xylene, etc., 134, 135)[q]		
X = H	> 196.6	> 197
X = Me	167.4 ± 4.2	167 ± 4
X = CH_2SiMe_3	142.3 ± 4.2	142 ± 4
X = Ph	154.8 ± 4.2	155 ± 4
X = Bz	159.0 ± 4.2	159 ± 4
X = CCPh	175.7 ± 4.2	176 ± 4
X = CH_2COMe	150.6 ± 4.2	151 ± 4
X = OH	121.3 ± 4.2	121 ± 4
X = OPh	138.1 ± 4.2	138 ± 4
X = NHPh	117.2 ± 4.2	117 ± 4
X = NPh_2	96.2 ± 4.2	96 ± 4
X = SH	138.1 ± 4.2	138 ± 4
X = SPh	133.9 ± 4.2	134 ± 4
X = Cl	138.1 ± 4.2	138 ± 4
X = Br	150.6 ± 4.2	151 ± 4
X = I	150.6 ± 4.2	151 ± 4
Group 9		
 19 (soln) =  20 (soln) + PPh_3(soln) (ES, toluene, 136)	48.5 ± 2.1	
Rh(acac)(cot)(soln) + $2P(OPh)_3$(soln) = $Rh(acac)[P(OPh)_3]_2$(soln) + cot(soln) (RSC, S, 137)		
S = CCl_4	−118.4 ± 2.9	
S = CH_2Cl_2	−107.9 ± 2.5	

TABLE 7 (*continued*)

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
Rh(acac)(cod)(soln) + 2P(OPh)$_3$(soln) = Rh(acac)[P(OPh)$_3$]$_2$(soln) + cod(soln) [RSC, S, 137)		
S = CCl$_4$	−99.6 ± 2.5	
S = CH$_2$Cl$_2$	−90.4 ± 2.1	
[Rh(X)(cod)]$_2$(soln) + 2PPh$_3$(soln) = 2Rh(X)(cod)PPh$_3$(soln) (RSC, CH$_2$Cl$_2$, 138)		
X = Cl	−114.2 ± 1.3	
X = Br	−121.8 ± 0.4	
X = I	−127.2 ± 1.7	
[Rh(X)(cod)]$_2$(soln) + 2P(OPh)$_3$(soln) = Rh$_2$(X)$_2$(cod)[P(OPh)$_3$]$_2$(soln) + cod(soln) (RSC, CH$_2$Cl$_2$, 138)		
X = Cl	−118.0 ± 2.1	
X = Br	−125.9 ± 2.1	
X = I	−126.4 ± 3.8	
Rh$_2$(X)$_2$(cod)[P(OPh)$_3$]$_2$(soln) + 2P(OPh)$_3$(soln) = {Rh(X)[P(OPh)$_3$]$_2$}$_2$(soln) + cod(soln) (RSC, CH$_2$Cl$_2$, 138)		
X = Cl	−98.3 ± 1.7	
X = Br	−104.6 ± 1.7	
X = I	−102.9 ± 0.8	
{Rh(X)[P(OPh)$_3$]$_2$}$_2$(soln) + 2P(OPh)$_3$(soln) = 2Rh(X)[P(OPh)$_3$]$_3$(soln) (RSC, CH$_2$Cl$_2$, 138)		
X = Cl	−98.7 ± 2.1	
X = Br	−97.9 ± 1.7	
X = I	−96.2 ± 1.3	
[Rh(Cl)(L)]$_2$(soln) + 2P(OPh)$_3$(soln) = Rh$_2$(Cl)$_2$(L)[P(OPh)$_3$]$_2$(soln) + L(soln) (RSC, CH$_2$Cl$_2$, 137)		
L = nbd	−117.6 ± 2.9	
L = cot	−115.5 ± 2.9	
L = dcpd	−119.2 ± 2.9	
Rh$_2$(Cl)$_2$(L)[P(OPh)$_3$]$_2$(soln) + 2P(OPh)$_3$(soln) = {Rh(Cl)[P(OPh)$_3$]$_2$}$_2$(soln) + L(soln) (RSC, CH$_2$Cl$_2$, 137)		
L = nbd	−94.6 ± 2.5	
L = cot	−105.4 ± 2.5	
L = dcpd	−110.0 ± 2.9	
L = C$_6$H$_4$O$_2$	−140.2 ± 3.3	
[Rh(Cl)(coct)$_2$]$_2$(soln) + 2P(OPh)$_3$(soln) = Rh$_2$(Cl)$_2$[P(OPh)$_3$]$_2$(coct)$_2$(soln) + 2coct(soln) (RSC, CH$_2$Cl$_2$, 137)	−133.1 ± 3.3	
Rh$_2$(Cl)$_2$[P(OPh)$_3$]$_2$(coct)$_2$(soln) + 2P(OPh)$_3$(soln) = {Rh(Cl)[P(OPh)$_3$]$_2$}$_2$(soln) + 2coct(soln) (RSC, CH$_2$Cl$_2$, 137)	−126.8 ± 3.3	
Group 10		
Ni(cod)$_2$(soln) + 2L(l) = NiL$_2$(cod)(soln) + cod(soln) (RSC, toluene, 139)		
L = P(O–*o*-Tol)$_3$	−83.7 ± 4.2	146 ± 2[r]
L = P(O–*o*-C$_6$H$_4$–i-Pr)$_3$	−62.8 ± 4.2	136 ± 2[r]

TABLE 7 (*continued*)

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
$Ni(cod)_2$(soln) + 3L(l) = NiL_3(soln) + 2cod(soln) (RSC, toluene, 139)		
L = PEt_3	-71.1 ± 4.2	163 ± 2[r]
L = PBu_3	-71.1 ± 4.2	163 ± 2[r]
L = PPh_3	-33.5 ± 4.2	150 ± 2[r]
L = $PPhEt_2$	-62.8 ± 4.2	160 ± 2[r]
$Ni(cod)_2$(soln) + 4L(l) = NiL_4(soln) + 2cod(soln) (RSC, toluene, 139)		
L = PMe_3	-150.6 ± 4.2	142 ± 2[r]
L = $PPhMe_2$	-159.0 ± 4.2	144 ± 2[r]
L = PPh_2Me	-133.9 ± 4.2	138 ± 2[r]
L = $PPh_2(OMe)$	-192.5 ± 4.2	153 ± 2[r]
L = $PPh(OEt)_2$	-238.5 ± 4.2	164 ± 2[r]
L = $P(OMe)_3$	-213.4 ± 4.2	158 ± 2[r]
L = $P(OEt)_3$	-200.8 ± 4.2	155 ± 2[r]
L = P(O–i-Pr)$_3$	-184.1 ± 4.2	150 ± 2[r]
L = $P(OPh)_3$	-163.2 ± 4.2	145 ± 2[r]
L = P(O–*p*-Tol)$_3$	-150.6 ± 4.2	142 ± 2[r]
L = $P(OCH_2CH_2Cl)_3$	-200.8 ± 4.2	155 ± 2[r]
NiL_4(soln) = NiL_3(soln) + L(soln) (ES, benzene, 141, 142)		
L = PEt_3	66.9 ± 8.4	67 ± 8
L = P(O–i-Pr)$_3$	98.3 ± 6.3	98 ± 6
L = P(O–*o*-Tol)$_3$	54.4 ± 6.3	54 ± 6
L = P(O–*p*-Tol)$_3$	96.2 ± 12.6	96 ± 13
L = P(O–2,4-$C_6H_3Me_2$)$_3$	50.2 ± 8.4	50 ± 8
L = P(O–*p*-C_6H_4Cl)$_3$	87.9 ± 29.3	88 ± 29
L = P(O–2-Me-4-Cl-C_6H_3)$_3$	52.3 ± 4.2	52 ± 4
Ni[P(O–*o*-Tol)$_3$]$_4$(soln) = Ni[P(O–*o*-Tol)$_3$]$_3$(soln) + P(O–*o*-Tol)$_3$(soln) (ES, toluene, 143)	71.1 ± 2.1	71 ± 2
Ni[P(O–*o*-Tol)$_3$]$_4$(soln) + C_2H_4(soln) = Ni[P(O–*o*-Tol)$_3$]$_3$(C_2H_4)(soln) + P(O–*o*-Tol)$_3$(soln) (ES, toluene, 143)	-17.2 ± 4.2	
Ni[P(O–*o*-Tol)$_3$]$_2$(C_2H_4)(soln) + P(O–*o*-Tol)$_3$(soln) = Ni[P(O–*o*-Tol)$_3$]$_3$(C_2H_4)(soln) (ES, toluene, 143)	-53.1 ± 4.2	53 ± 4
Ni[P(O–*o*-Tol)$_3$]$_3$(soln) + C_2H_4(soln) = Ni[P(O–*o*-Tol)$_3$]$_2$(C_2H_4)(soln) + P(O–*o*-Tol)$_3$(soln) (ES, benzene, 144)	-14	
$Ni(PR_3)_4$(soln) + L(soln) = $Ni(PR_3)_2L$(soln) + $2PR_3$(soln) (ES, benzene, 145)		
L = Cy PR_3 = P(O–*p*-Tol)$_3$	142.3 ± 20.9	
L = Hex PR_3 = P(O–*p*-Tol)$_3$	96.2 ± 4.2	
L = CH_2CHCN PR_3 = P(O–*p*-Tol)$_3$	77.4 ± 6.3	
L = maa PR_3 = P(O–*p*-Tol)$_3$	50.2 ± 6.3	
L = Hex PR_3 = P(O–*p*-C_6H_4Cl)$_3$	108.8 ± 8.4	
L = CH_2CHCN PR_3 = P(O–*p*-C_6H_4Cl)$_3$	77.4 ± 6.3	
L = maa PR_3 = P(O–*p*-C_6H_4Cl)$_3$	62.8 ± 4.2	

TABLE 7 (*continued*)

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
$[Ni(\eta^3\text{-}MeC_3H_3Me)]_2(\mu\text{-}Me)_2(soln) + 2L(soln) = 2Ni(\eta^3\text{-}MeC_3H_3Me)(Me)L(soln)$ (DTA, tetralin, 146)		
L = PMe_3	−120 ± 4	L7[s]
L = PEt_3	−108 ± 4	L7 − (6 ± 6)[s]
L = PPr_3	−106 ± 4	L7 − (7 ± 6)[s]
L = $P(i\text{-}Pr)_3$	−88 ± 4	L7 − (16 ± 6)[s]
L = PBu_3	−105 ± 4	L7 − (8 ± 6)[s]
L = PPh_3	−112 ± 4	L7 − (4 ± 6)[s]
L = PBz_3	−97 ± 4	L7 − (12 ± 6)[s]
L = $P(i\text{-}Pr)_2(t\text{-}Bu)$	−82 ± 4	L7 − (19 ± 6)[s]
L = $PPhMe_2$	−116 ± 4	L7 − (2 ± 6)[s]
L = $PPhEt_2$	−109 ± 4	L7 − (6 ± 6)[s]
L = $P(t\text{-}Bu)Cy_2$	−77 ± 4	L7 − (22 ± 6)[s]
L = PPh_2Et	−111 ± 4	L7 − (5 ± 6)[s]
L = $PPh_2(OEt)$	−123 ± 4	L7 + (2 ± 6)[s]
L = $PPh(OPh)_2$	−136 ± 4	L7 + (8 ± 6)[s]
L = $PPh(OMen)_2$	−121 ± 4	L7 + (1 ± 6)[s]
L = $P(OEt)_3$	−144 ± 4	L7 + (12 ± 6)[s]
L = $P(O\text{–}i\text{-}Pr)_3$	−131 ± 4	L7 + (6 ± 6)[s]
L = $P(OBu)_3$	−142 ± 4	L7 + (11 ± 6)[s]
L = $P(OPh)_3$	−149 ± 4	L7 + (15 ± 6)[s]
L = $P(OMen)_3$	−125 ± 4	L7 + (3 ± 6)[s]
L = $P(O\text{–}o\text{-}Tol)_3$	−140 ± 4	L7 + (10 ± 6)[s]
L = $P(O\text{–}o\text{-}C_6H_4Ph)_3$	−135 ± 4	L7 + (8 ± 6)[s]
$Pd(Cl)_2(PhCN)_2(soln) + diphos(soln) =$ $Pd(Cl)_2diphos(soln) + 2PhCN(soln)$ (RSC, CH_2Cl_2, 147)	−211.3 ± 7.1	L8[t]
$Pd(Cl)_2(PhCN)_2(soln) + 2PPh_3(soln) =$ $Pd(Cl)_2(PPh_3)_2(soln) + 2PhCN(soln)$ (RSC, CH_2Cl_2, 138)	−163.2 ± 4.6	L8 − (24 ± 4)[t,u]
$Pd(Cl)_2(cod)(soln) + 2P(OPh)_3(soln) =$ $Pd(Cl)_2[P(OPh)_3]_2(soln) + cod(soln)$ (RSC, CH_2Cl_2, 138)	−88.7 ± 2.1	
trans-$Pd(PPh_3)_2(Cl)(COCOPh)(soln) =$ $Pd(PPh_3)(Cl)(COCOPh)(soln) + PPh_3(soln)$ (ES, CH_2Cl_2, 148)	54.4 ± 2.9	
$Pt(PCy_3)_3(soln) = Pt(PCy_3)_2(soln) + PCy_3(soln)$ (ES, toluene, 56)	54.8 ± 2.1	55 ± 2
$Pt(Cl)_2(py)(C_2H_4)(soln) + P(OPh)_3(l) = Pt(Cl)_2(py)[P(OPh)_3](soln) + C_2H_4(soln)$ (RSC, S, 149)		
S = benzene	−58 ± 1	
S = CH_2Cl_2	−58 ± 1	
$Pt(Cl)_2(py)[P(OPh)_3](soln) + P(OPh)_3(l) =$ $Pt(Cl)_2[P(OPh)_3]_2(soln) + py(soln)$ (RSC, benzene, 149)	−44.2 ± 0.6	

TABLE 7 (*continued*)

Reaction (method, solvent, reference)[a,b]	ΔH_r	D(M–P)[c]
[*trans*-Pt(PPhMe$_2$)$_2$(Me)(thf)]PF$_6$(soln) + L(soln) = [*cis*/*trans*-Pt(PPhMe$_2$)$_2$(Me)(L)]PF$_6$(soln) + thf(soln) (RSC, thf, 150)		
L = PMe$_3$	−109.6 ± 2.1	L9^v
L = PEt$_3$	−101.7 ± 2.1	L9 − (8 ± 3)^v
L = P(i-Pr)$_3$	−53.1 ± 2.1	L9 − (57 ± 3)^v
L = P(*t*-Bu)$_3$	−20.1 ± 2.1	L9 − (90 ± 3)^v
L = PPh$_3$	−81.6 ± 2.1	L9 − (28 ± 3)^v
L = P(*o*-Tol)$_3$	−7.9 ± 2.1	L9 − (102 ± 3)^v
L = PCy$_3$	−66.5 ± 2.1	L9 − (43 ± 3)^v
L = PBz$_3$	−97.1 ± 2.1	L9 − (13 ± 3)^v
L = PPhMe$_2$	−104.6 ± 2.1	L9 − (5 ± 3)^v
L = PPh$_3$Me	−92.5 ± 2.1	L9 − (17 ± 3)^v
L = P(CH$_2$CH$_2$CN)$_3$	−73.6 ± 2.1	L9 − (36 ± 3)^v
L = P(OMe)$_3$	−110.5 ± 2.1	L9 + (1 ± 3)^v
L = P(OEt)$_3$	−105.4 ± 2.1	L9 − (4 ± 3)^v
L = P(O–i-Pr)$_3$	−104.2 ± 2.1	L9 − (5 ± 3)^v
L = P(O–*t*-Bu)$_3$	−74.9 ± 2.1	L9 − (35 ± 3)^v
L = P(OPh)$_3$	−89.5 ± 2.1	L9 − (20 ± 3)^v
L = P(O–*o*-Tol)$_3$	−80.8 ± 2.1	L9 − (29 ± 3)^v
L = P(O–2,6-C$_6$H$_3$Me$_2$)$_3$	−2.1 ± 2.1	L9 − (108 ± 3)^v
L = P(O–*o*-C$_6$H$_4$-i-Pr)$_3$	−71.5 ± 2.1	L9 − (38 ± 3)^v
L = P(O–*o*-C$_6$H$_4$-*t*-Bu)$_3$	−38.1 ± 2.1	L9 − (72 ± 3)^v
L = P(O–*o*-C$_6$H$_4$Ph)$_3$	−74.5 ± 2.1	L9 − (35 ± 3)^v
L = P(O–*p*-C$_6$H$_4$OMe)$_3$	−89.1 ± 2.1	L9 − (21 ± 3)^v
L = P(O–*o*-C$_6$H$_4$CN)$_3$	−78.7 ± 2.1	L9 − (31 ± 3)^v
L = P(OCH$_2$CH$_2$Cl)$_3$	−110.5 ± 2.1	L9 + (1 ± 3)^v
L = P(OCH$_2$CCl$_3$)$_3$	−81.2 ± 2.1	L9 − (28 ± 3)^v
L = Me$_2$PCH$_2$CH$_2$PMe$_2$	−116.3 ± 2.1	L9 + (7 ± 3)^v
L = P(OCH$_2$)$_3$CCH$_2$CH$_2$Me	−110.0 ± 2.1	L9 + (0 ± 3)^v
Group 11		
Ag(hfacac)(cod)(soln) + PPh$_3$(soln) = Ag(hfacac)(PPh$_3$)(soln) + cod(soln) (RSC, CH$_2$Cl$_2$, 151)	−49.0 ± 0.8	
Ag(hfacac)(PPh)$_3$(soln) + PPh$_3$(soln) = Ag(hfacac)(PPh$_3$)$_2$(soln) (RSC, CH$_2$Cl$_2$, 151)	−47.3 ± 0.4	47 ± 1

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[a] DTA = Differential thermal analysis; EC = electrocalorimetry; ES = equilibrium studies in solution; KS = kinetic studies in solution; PAC = photoacoustic calorimetry; RSC = reaction–solution calorimetry.

acac = acetylacetonate; C$_6$H$_4$O$_2$ = *p*-benzoquinone; C$_6$H$_9$ = 3-methylpentadienyl; C$_7$H$_{11}$ = 2,4-dimethylpentadienyl; coct = cyclo-octene; cod = 1,5-cyclo-octadiene; cot = 1,3,5,7,-cyclo-octatetraene; Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; Cy = cyclohexyl; dcpd = dicyclopentadiene; dede = bis(β-ethoxyethyl)ether; diphos = (Ph$_2$PCH$_2$)$_2$; hfacac = hexafluoroacetylacetonate; Hex = hexyl; maa = maleic anhydride; Men = menthyl; nbd = norbornadiene; py = pyridine; thf = tetrahydrofuran; Tol = tolyl; triphos = Ph$_2$PCH$_2$CH$_2$PPhCH$_2$CH$_2$PPh$_2$.

TABLE 7 (*continued*)

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[b] See text for further details.

[c] Bond dissociation enthalpies, unless indicated otherwise.

[d] Relies on $D(\text{P–H}) = 323\ \text{kJ mol}^{-1}$.

[e] Relies on $D[(\text{CO})_5\text{Cr–CO}] = 154 \pm 13\ \text{kJ mol}^{-1}$.

[f] Relies on $D(\text{Cr–heptane}) = 41\ \text{kJ mol}^{-1}$.

[g] $\text{L1} = D[\text{Mo(Cp)(CO)}_2\text{(H)–CO}]$.

[h] L2, L3, $\text{L4} = D[\text{Mo(Cp)(CO)}_3\text{–R}] + D[\text{Mo(Cp)(CO)}_2\text{–CO}] - D[\text{C(O)–R}] - D[\text{Mo(Cp)(CO)}_2\text{–C(O)R}]$ for R = Me, Et, Bz, respectively.

[i] The reaction enthalpies were calculated from the enthalpies of the two previous reactions. See text. $\text{L5} = \bar{D}(\text{Mo–CO})$ in $[\text{Mo(Cp)(CO)}_3]_2$.

[j] Mean bond dissociation enthalpy. It relies on $D(\text{Mo–PhMe}) = 257\ \text{kJ mol}^{-1}$.

[k] Low values due to the formation of $\text{M(L)}_2\text{(CO)}_3$.

[l] See text. Mean bond dissociation enthalpy.

[m] Mean bond dissociation enthalpy. It relies on $D[(\text{CO})_5\text{Mo–CO}] + D[(\text{CO})_4\text{Mo–CO}] = 316\ \text{kJ mol}^{-1}$.

[n] Mean bond dissociation enthalpy. It relies on $D(\text{Mo–nbd}) = 221\ \text{kJ mol}^{-1}$.

[o] Relies on $D(\text{Mo–nbd}) = 221\ \text{kJ mol}^{-1}$.

[p] $\text{L6} = D(\text{W–PhNH}_2)$.

[q] These values are activation enthalpies and were identified with Ru–PMe_3 bond dissociation enthalpies. See text.

[r] Mean bond dissociation enthalpy. It relies on $\bar{D}(\text{Ni–cod}) = 209 \pm 2\ \text{kJ mol}^{-1}$. See text.

[s] $\text{L7} = D(\text{Ni–PMe}_3)$.

[t] $\text{LS} = D(\text{Pd–diphos})/2$.

[u] Mean bond dissociation enthalpy.

[v] $\text{L9} = D(\text{Pt–PMe}_3)$.

compounds. A group additivity method has been proposed to estimate enthalpies of vaporization of phosphorus compounds, including alkyl phosphines [115]. A large number of enthalpies of vaporization/sublimation of phosphorus(III) compounds has also been estimated from correlations of ΔH_v^0 or ΔH_s^0 with enthalpies of solution and molar refractions in several solvents [116].

In conclusion, the thermochemical data for organophosphorus(III) compounds are scarce and in many cases of low accuracy, hindering reliable estimates of new values. A considerable number of phosphines commonly used in organometallic chemistry, such as tricyclohexylphosphine and triisopropylphosphine, were never investigated. The use of rotating-bomb and reaction–solution calorimetry together with modern analytical techniques, such as ionic chromatography, may contribute to change the present situation.

4.2 Thermochemical data of organometallic compounds containing phosphorus ligands

Thermochemical values which provide information on the energetics of metal–phosphorus bonds are presented in Tables 7 and 8. The first of these tables collects enthalpy of reaction data and the second the available enthalpies of formation of complexes containing phosphorus(III) ligands. Some of the data in both tables differ from those originally reported by the authors due to the use of different auxiliary thermochemical values (Table 6 and Appendix). A general discussion of data is made in Sect. 4.2.3.

4.2.1 Reaction enthalpy data

A general assumption that affects all bond dissociation enthalpies in Table 7 is related to the experimental techniques used to probe the energetics of the reactions, usually reaction–solution calorimetry and equilibrium methods. Both techniques deal with reactants and products in solution and therefore the measured enthalpies include the solvation of those molecules. No attempt has been made to estimate the unknown solvation enthalpies required to calculate the reaction and the bond dissociation enthalpies in the gas phase, i.e. the bond dissociation enthalpies were directly derived from the experimental reaction enthalpies given in Table 7. A detailed discussion of this problem has been made elsewhere [117] and it is expected that many of those values are close to the gas-phase data. It must be stressed, however, that there is almost no solid evidence supporting this assumption. Even in the most favourable cases, probably those involving a comparison of the enthalpies of similar reactions, some caution has to be used when trying to identify solution and gas-phase data. Nevertheless, solution values of bond dissociation enthalpies are useful by themselves, so for many applications one does not need to worry about the above assumption.

Lanthanides. The only lanthanide–phosphorus bond dissociation enthalpy available, $D(\text{Sm–PEt}_2) = 136 \pm 8$ kJ mol^{-1}, was determined by Nolan et al. [118] and relies on $D(\text{Sm–H}) = 226 \pm 4$ kJ mol^{-1} and an estimate for $D(\text{Et}_2\text{P–H})$ (323 kJ mol^{-1}) [118]. Differences between metal–ligand bond dissociation enthalpies often reflect the corresponding ligand–hydrogen bond dissociation enthalpy differences (see, for example, ref. 117 and the references cited therein). On this basis, it is noted, with Nolan et al., that the above estimate for $D(\text{Et}_2\text{P–H})$ is some 59 kJ mol^{-1} lower than the experimental value for $D(\text{Me}_2\text{N–H})$ [119], suggesting that $D(\text{Sm–NMe}_2)$ in the diamide complex would be ca. 195 kJ mol^{-1}. This is indeed quite close to the samarium–dimethylamide bond dissociation enthalpy in $\text{Sm(Cp}^*)_2\text{NMe}_2$, 185 ± 11 kJ mol^{-1}, obtained by the same authors.

Group 4. The enthalpies of ligand dissociation measured by Stahl and Ernst [49], involving several bis(pentadienyl) titanium complexes, yield direct information on the energetics of Ti–P bonds in thf (Table 7). The stronger Ti–PEt_3 bond in the 3-methylpentadienyl complex, 61 kJ mol^{-1}, compared with the same bond in the 2,4-dimethylpentadienyl molecule, 42 kJ mol^{-1}, was justified by the authors in terms of interligand Me–Me repulsive interactions in the case of the latter complex. The authors' re-evaluation of Tolman's cone angles for P(OMe)_3 (128°), P(OEt)_3 (134°), and PEt_3 (137°) (see Table 1) led, on the other hand, to a good linear correlation between $D(\text{Ti–P})$ and those steric parameters.

Group 6. The enthalpy of the second reaction for this group listed in Table 7 was derived by Wovkulich and Atwood from measurements of rate constants at three temperatures [120]. According to the principle of microscopic reversibility, the energy profile of the forward reaction is the reverse of the profile for the replacement of CO by L. This assumption was used by the authors together with the activation enthalpies of L and CO dissociation (PPh_3, 151.9 ± 7.9 kJ mol^{-1}; $P(OPh)_3$, 133.5 ± 4.6 kJ mol^{-1}; CO, 168.2 ± 2.5 kJ mol^{-1} in hexane) to derive the reaction enthalpies shown in Table 7. These can in turn be identified with the difference $D(Cr{-}P) - D(Cr{-}CO)$. The Cr–P bond dissociation enthalpies shown rely on $D[(CO)_5Cr{-}CO] = 154 \pm 13$ [121]. A value which is not presented in Table 7 refers to $L = PBu_3$ and was obtained from the equilibrium constants determined by Wovkulich and Atwood in decane (1.3×10^{-4} (170°C) and 5.3×10^{-5} (140°C)) [120]. This leads to a crude estimate of the reaction enthalpy, 45 kJ mol^{-1}, and to $D(Cr{-}PBu_3) \approx 199$ kJ mol^{-1}, which looks too high. This is indeed confirmed by the result in Table 7, obtained by Yang et al. who used photoacoustic calorimetry to probe the energetics of CO replacement by tributhylphosphine in heptane [122]. This technique affords both the enthalpy of the CO replacement by heptane and the enthalpy of replacement of this solvent molecule by the phosphine. An average value of the first step, 112.9 ± 1.0 kJ mol^{-1}, together with the above value for $D[(CO)_5Cr{-}CO]$ (154 ± 13 kJ mol^{-1}), leads to $D(Cr{-}heptane) = 41 \pm 13$ kJ mol^{-1}. This result was then used to derive $D(Cr{-}PBu_3) = 131 \pm 14$ kJ mol^{-1} shown in Table 7.

A significant contribution to the knowledge of metal–phosphorus bonding energetics for Group 6 elements was provided by the reaction–solution calorimetry studies by Hoff and co-workers [123–128]. Many of these studies involve the complexes $Mo(Cp)(CO)_3R$, where R = H, Me, Et, and Bz. In the case of R = H, the enthalpies of reaction of the complex with a number of phosphorus(III) ligands, L, yielding $Mo(Cp)(CO)_2(L)H$ and CO, can be identified with $D(Mo{-}CO) - D(Mo{-}L)$. However, $D(Mo{-}CO)$ in $Mo(Cp)(CO)_3H$ is not available, so only the trend of $D(Mo{-}L)$, relative to $D(Mo{-}CO) = L1$ is displayed in Table 7.

When R = Me, Et, or Bz, the reaction of $Mo(Cp)(CO)_3R$ with the phosphorus ligand L promotes the CO insertion into the Mo–R bond, so that the reaction enthalpies are now given by $D[Mo(Cp)(CO)_3{-}R] + D[Mo(Cp)(CO)_2{-}CO] - D[C(O){-}R] - D[Mo(Cp)(CO)_2{-}C(O)R] - D[Mo(Cp)(CO)_2C(O)R{-}L]$. While many of these quantities are unknown, they are constant for each R, allowing the relative values of $D[Mo(Cp)(CO)_2C(O)R{-}L]$ presented in Table 7 to be derived.

The enthalpy of reaction of the dimer $[Mo(Cp)(CO)_2]_2$ with CO, giving $[Mo(Cp)(CO)_3]_2$ (−168.6 ± 1.4 kJ mol^{-1}), was subtracted from enthalpies for the reaction of the same complex with PPh_2Me and $P(OMe)_3$ (Table 7) to yield the enthalpies of the ligand exchange reactions involving $[Mo(Cp)(CO)_3]_2$ and $[Mo(Cp)(CO)_2L]_2$, also shown in Table 7. These enthalpies can be identified with the mean bond dissociation enthalpy difference $2\bar{D}(Mo{-}CO) - 2\bar{D}(Mo{-}L)$. L5 in Table 7 represents $\bar{D}(Mo{-}CO)$. It is noted that the two calculated values are smaller than $\bar{D}$(Mo–CO), in contrast to what is observed for the previous families of Mo(Cp)$(CO)_3$R complexes. As pointed out by Hoff and co-workers, this trend may be due to steric strain in the dimer [126].

The energetics of replacing the η^6-toluene in $Mo(CO)_3(PhMe)$ by three phosphines or phosphites were measured by Nolan and Hoff [123]. The results are displayed in Table 7 and, together with $D(\text{Mo–PhMe}) = 257 \pm 44$ kJ mol^{-1}, were used to derive the $\bar{D}$(Mo–P) values shown in Table 7. The value of D(Mo–PhMe) was obtained as follows. The enthalpy of reaction (15) (Mes = mesitylene) 175.7 ± 14.0 kJ mol^{-1}, was calculated from tabulated enthalpies of formation [110,129]. Recent molecular beam experiments led to several stepwise Mo–CO bond dissociation enthalpies in molybdenum hexacarbonyl, the sum of the first three being 439 ± 44 kJ mol^{-1} [130]. This value and the enthalpy of reaction (15) yield $D(\text{Mo–Mes}) = 263 \pm 44$ kJ mol^{-1}, which can in turn be used, together with the enthalpy of reaction (16) (6.3 ± 5.2 kJ mol^{-1}), determined by Hoff [131], to calculate $D(\text{Mo–PhMe}) = 257 \pm 44$ kJ mol^{-1}. This uncertainty interval is not included in the errors assigned to the mean bond dissociation enthalpies in Table 7.

$$Mo(CO)_6(g) + Mes(g) = Mo(CO)_3(Mes)(g) + 3CO(g) \qquad (15)$$

$$Mo(CO)_3(Mes)(soln) + PhMe(soln) = Mo(CO)_3(PhMe)(soln) + Mes(soln) \qquad (16)$$

Nolan and Hoff justified the very low exothermic values observed for the reactions with L = P(t-Bu)$_3$ and PCy$_3$ by the formation of the disubstituted coordinatively unsaturated complexes, $Mo(CO)_3L_2$, which may yield an adduct with a solvent (thf) molecule. Maximum values of $\bar{D}$(Mo–L) in these cases can be calculated by neglecting this interaction with the solvent and using $D(\text{Mo–PhMe}) = 257$ kJ mol^{-1}: $\bar{D}(\text{Mo–L}) = 149$ and 173 kJ mol^{-1} for L = P(t-Bu)$_3$ and PCy$_3$, respectively.

The enthalpy of reaction of molybdenum hexacarbonyl with PPh$_2$Me in bis(β-ethoxyethyl)ether was used to calculate the Mo–PPh$_2$Me mean bond dissociation enthalpy in $Mo(CO)_4(PPh_2Me)_2$ by taking $D[(CO)_5\text{Mo–CO}] + D[(CO)_4\text{Mo–CO}] = 316$ kJ mol^{-1} [130]. The error assigned to the value shown in Table 7 (161 ± 4 kJ mol^{-1}) does not include the uncertainty in the sum of the Mo–CO bond enthalpies. As noted by Hoff and co-workers [124], the difference in $\bar{D}(\text{Mo–CO}) - \bar{D}(\text{Mo–PPh}_2\text{Me})$ in these complexes of -7 kJ mol^{-1} is similar to that derived for the trisubstituted complex $Mo(CO)_3(PPh_2Me)_3$ discussed above, $\bar{D}(\text{Mo–CO}) - \bar{D}(\text{Mo–PPh}_2\text{Me}) = 4$ kJ mol^{-1} (the uncertainties due to the assumptions related to solvation enthalpies are at least 10 kJ mol^{-1}).

The two final series of molybdenum complexes shown in Table 7 involve the reactions of the norbornadiene complex $Mo(CO)_4$(nbd) with several phosphines and phosphites [125]. In the first of those series, the Mo–L mean bond dissociation enthalpies presented were derived by taking the enthalpy of reaction (17) and the above sum of the first two Mo–CO bond dissociation enthalpies in $Mo(CO)_6$, 316 kJ mol^{-1} (once again the error of this anchor was not considered).

$$Mo(CO)_4(nbd)(g) + 2CO(g) = Mo(CO)_6(g) + nbd(g) \qquad (17)$$

Two values for the enthalpy of this reaction are available in the literature. One, -112.8 ± 11.4 kJ mol^{-1}, is calculated from the enthalpies of formation [110,129], and leads to D(Mo–nbd) = 203 kJ mol^{-1}. The other, -94.6 ± 3.3 kJ mol^{-1}, yielding D(Mo–nbd) = 221 kJ mol^{-1}, was measured in thf solution by high-pressure calorimetry [125]. It is possible that the discrepancy of 18 kJ mol^{-1} results from differential solvation enthalpies, but since the reactions in Table 7 were studied in solution, the second value was adopted here.

The last series of molybdenum complexes in Table 7 is similar to the previous series, but norbornadiene is replaced by one bidentate phosphine. The bond dissociation enthalpies rely on the same basis, i.e. D(Mo–nbd) = 221 kJ mol^{-1}. A detailed discussion of both series of results was made by Hoff and co-workers in terms of steric and electronic properties of the ligands [125]. As noted by the authors, some of the bond dissociation enthalpies of the bidentate phosphines could be predicted from the values for the monodentate ligands. For example, $D(\mathrm{Mo{-}Me_2PCH_2CH_2PMe_2})/2 = 179$ kJ mol^{-1} is similar to $\bar{D}(\mathrm{Mo{-}PMe_3})$, and $D[\mathrm{Mo{-}Ph_2P(CH_2)_3PPh_2}]/2 = 159$ kJ mol^{-1} is similar to $\bar{D}(\mathrm{Mo{-}PPh_2Me})$. On the other hand, low values such as $D(\mathrm{Mo{-}Me_2PCH_2PMe_2})/2 = 162$ kJ mol^{-1}, and $D(\mathrm{Mo{-}Ph_2PCH_2PPh_2})/2 = 144$ kJ mol^{-1} indicate strain in the metallacycle. It is finally noted that the bond dissociation enthalpy obtained for $\mathrm{L = Ph_2PCH_2CH_2AsPh_2}$ (302 kJ mol^{-1}) is close to the average between $D(\mathrm{Mo{-}Ph_2PCH_2CH_2PPh_2})$ and $D(\mathrm{Mo{-}Ph_2AsCH_2CH_2AsPh_2})$ (this one included for comparison), 323 and 271 kJ mol^{-1}, respectively.

The metal–P(OMe)$_3$ bond dissociation enthalpies in the complexes $\mathrm{M(CO)_3(PCy_3)_2P(OMe)_3}$ (M = Cr, Mo, W), shown in Table 7, are rather low (compared, for example, with the bond enthalpies derived for several molybdenum complexes). As pointed out by Hoff and co-workers, the low exothermicities of the reactions are due to the cleavage of M··H–C agostic bonds in the molecules $\mathrm{M(CO)_3(PCy_3)_2}$ upon formation of $\mathrm{M(CO)_3(PCy_3)_2P(OMe)_3}$ [127,128].

The enthalpy of reaction between $\mathrm{W(CO)_3(PCy_3)_2(H_2)}$ and P(OMe)$_3$ is also constant for the two solvents used and can yield $D(\mathrm{W{-}H_2}) = 40 \pm 2$ kJ mol^{-1} when taken together with the enthalpy of the previous reaction, e.g. in toluene $D(\mathrm{W{-}H_2}) = -67.8 + 110.9 = 43.1$ kJ mol^{-1}. The value of 40 kJ mol^{-1} chosen for $D(\mathrm{W{-}H_2})$ is an average involving the enthalpies of reaction of $\mathrm{W(CO)_3(PCy_3)_2}$ and $\mathrm{W(CO)_3(PCy_3)_2(H_2)}$ with P(OMe)$_3$ and pyridine in toluene and thf. The W–P(OMe)$_3$ bond dissociation enthalpy can be compared with D(W–CO) because the enthalpy of reaction (18) is available: -85.8 ± 2.9 kJ mol^{-1} (toluene) and -95.4 ± 4.2 kJ mol^{-1} (thf) [127].

$$\mathrm{W(CO)_3(PCy_3)_2(H_2)(soln) + CO(soln) = W(CO)_4(PCy_3)_2(soln) + H_2(soln)} \qquad (18)$$

This reaction is more exothermic (by 18 and 30 kJ mol^{-1} in toluene and thf, respectively) than the equivalent reaction in Table 7 for P(OMe)$_3$, indicating that D(W–CO) is higher by ca. 25 kJ mol^{-1} than D[W–P(OMe)$_3$].

Equilibrium studies in solution by Angelici and Ingemanson afforded the data shown in Table 7 for the reactions between $W(CO)_5(PhNH_2)$ and several phosphines and phosphites [132]. $D(W\text{—}PhNH_2)$ is not available, so only the trend of $D(W\text{—}L)$ is displayed in Table 7.

Group 8. Boudeville and Darchen have used an electrocalorimeter to probe the reaction of $Fe(Cp)(arene)^+$ with $P(OMe)_3$ for several arenes [133]. The result for arene $= C_6H_6$ is shown in Table 7. However, $D(Fe\text{—}C_6H_6)$ is unknown, so $D(Fe\text{—}P)$ cannot be derived.

Activation enthalpies for the phosphine dissociation reactions of the complexes $Ru(Cp^*)(PMe_3)_2X$, for a variety of X, were reported by Bercaw and co-workers [134,135] and are collected in Table 7. A detailed discussion of these results is made by the authors and it is assumed that the activation enthalpies for the recombination of trimethylphosphine are small and relatively constant for different X. The trends of the activation enthalpies and $Ru\text{—}PMe_3$ bond dissociation enthalpies are therefore considered approximately parallel. As noted by the authors, however, bulky ligands X are expected to have larger activation barriers for PMe_3 recombination "so that the differences in the activation enthalpies for PMe_3 dissociation represent lower limits for the differences in $D(Ru\text{—}P)$" [135]. Nevertheless, it is in fact observed that, for ligands with negligible π interactions, $D(Ru\text{—}P)$ decreases with increasing bulkiness of X.

Group 9. The enthalpy of phosphine dissociation from a cobaltacyclopent-2-ene complex, leading to a cobaltoxanorbornadiene molecule, was obtained from a van't Hoff plot in toluene by Stolzenberg and Scozzafava [136], and reflects the difference $D(Co\text{—}PPh_3) - D(Co\text{—}O)$.

The available thermochemical information on rhodium–phosphorus bonds was derived by Partenheimer and Hoy [137,138]. The aim of these studies was, however, to probe the energetics of rhodium–olefin bonding by determining enthalpies of ligand exchange reactions. This is indeed the main information that can be derived from the data in Table 7, as discussed elsewhere [117]. For example, the series of data in Table 7 starts with reactions where cyclooctatetraene or cyclooctadiene are replaced by two triphenylphosphite ligands. As $D(Rh\text{—}cot)$ and $D(Rh\text{—}cod)$ are unknown, $\bar{D}(Rh\text{—}P)$ cannot be calculated, but $D(Rh\text{—}cot) - D(Rh\text{—}cod)$ are easily derived.

The four following sets of reactions start with the dimer $[Rh(X)(cod)]_2$ and PPh_3 or $P(OPh)_3$ (X = Cl, Br, I), and are repeated here for X = Cl (the subscripts brg and term represent bridging and terminal bonds):

$$[Rh(Cl)(cod)]_2(soln) + 2PPh_3(soln) = 2Rh(Cl)(cod)PPh_3(soln) \tag{19}$$

$$\Delta H/2 = -114.2/2 = 2D_{brg}(Rh\text{—}Cl) - D_{term}(Rh\text{—}Cl) - D(Rh\text{—}PPh_3) \tag{20}$$

$$\begin{aligned}&[Rh(Cl)(cod)]_2(soln) + 2P(OPh)_3(soln)\\&\quad = Rh_2(Cl)_2(cod)[P(OPh)_3]_2(soln) + cod(soln)\end{aligned} \tag{21}$$

$$\Delta H = -118.0 = D_1(\text{Rh–cod}) + 2\bar{D}[\text{Rh–P(OPh)}_3] \tag{22}$$

$$\text{Rh}_2(\text{Cl})_2(\text{cod})[\text{P(OPh)}_3]_2(\text{soln}) + 2\text{P(OPh)}_3(\text{soln})$$
$$= \{\text{Rh(Cl)}[\text{P(OPh)}_3]_2\}_2(\text{soln}) + \text{cod(soln)} \tag{23}$$

$$\Delta H = -98.3 = D_2(\text{Rh–cod}) - 2\bar{D}[\text{Rh–P(OPh)}_3] \tag{24}$$

$$\{\text{Rh(Cl)}[\text{P(OPh)}_3]_2\}_2(\text{soln}) + 2\text{P(OPh)}_3(\text{soln}) = 2\text{Rh(Cl)}[\text{P(OPh)}_3]_3(\text{soln}) \tag{25}$$

$$\Delta H/2 = -98.7/2 = 2D_{\text{brg}}(\text{Rh–Cl}) - D_{\text{term}}(\text{Rh–Cl}) - D[\text{Rh–P(OPh)}_3] \tag{26}$$

It is not possible to extract accurate values for the rhodium–triphenylphosphite bond enthalpies from these data. It is noted, however, that the second substitution of cod is less exothermic (by ca. 20 kJ mol^{-1}) than the first. On the other hand, if it is assumed that the complexes $[\text{Rh(Cl)(cod)}]_2$ and $\{\text{Rh(Cl)}[\text{P(OPh)}_3]_2\}_2$ have similar $D_{\text{brg}}(\text{Rh–Cl})$, and $D_{\text{term}}(\text{Rh–Cl})$ is constant in Rh(Cl)(cod)PPh_3 and $\text{Rh(Cl)}[\text{P(OPh)}_3]_3$, eqns. (20) and (26) lead to $D(\text{Rh–PPh}_3) - D[\text{Rh–P(OPh)}_3] = 8$ kJ mol^{-1}, which looks sensible (see the data for molybdenum complexes).

The thermochemistry of reactions (21) and (23) was also studied for other η^4-bonded olefins, as shown in Table 7, and, as above, it is not possible to extract information on the energetics of Rh–P(OPh)_3; only differences $D(\text{Rh–olefin}) - 2\bar{D}[\text{Rh–P(OPh)}_3]$ and relative trends of D(Rh–olefin) can be derived [117]. The same comment applies to the last pair of reactions for Group 9 complexes, involving the replacement of two η^2-olefins (cyclooctene) by P(OPh)_3.

Group 10. The enthalpies of the reactions of Ni(cod)_2 with two, three or four phosphorus(III) ligands (Table 7), measured by Tolman et al. [139], lead to trends of Ni–P mean bond dissociation enthalpies. The absolute values shown in Table 7 rely on $\bar{D}(\text{Ni–cod}) = 209 \pm 2$ kJ mol^{-1}, which was estimated from the measured enthalpy of reaction (27) in toluene [139], -12.6 ± 4.2 kJ mol^{-1}, together with the enthalpy of sublimation of nickel, 429.7 kJ mol^{-1} [140]. It is assumed, of course, that the solvation enthalpies of Ni(cod)_2 and two molecules of cod are similar.

$$\text{Ni(cod)}_2(\text{soln}) = \text{Ni(c)} + 2\text{cod(soln)} \tag{27}$$

The use of $\bar{D}$(Ni–cod) instead of D[(cod)Ni–cod] to derive $\bar{D}$(Ni–P) in the case of the reaction of Ni(cod)_2 with two phosphites is clearly an approximation and so these two mean bond dissociation enthalpies in Table 7 are not strictly comparable with those derived from the reactions with three or four ligands, where both Ni–cod bonds are cleaved. It is likely that D[(cod)Ni–cod] is lower than $\bar{D}$(Ni–cod), so that $\bar{D}[\text{Ni–P(O–}o\text{-Tol)}_3] < 146$ kJ mol^{-1} and $\bar{D}[\text{Ni–P(O–}o\text{-C}_6\text{H}_4\text{–i-Pr)}_3] < 136$ kJ mol^{-1}, in keeping with the cone angles for these phosphites (Table 1). The conclusion seems consistent, for example, with the values observed for $\bar{D}[\text{Ni–P(O–}p\text{-Tol)}_3]$ (142 kJ mol^{-1}), and $\bar{D}[\text{Ni–P(OPh)}_3]$ (145 kJ mol^{-1}). The cone angle of $\text{P(O–}o\text{-Tol)}_3$ (141°) is significantly higher than the cone angles of $P(O\text{–}p\text{-Tol})_3$ and $P(OPh)_3$ (both 128°; note, however, that the cone angles reported by Trogler and Marzilli [50,51] are identical (128°) for the three latter phosphites; see Table 1). Assuming similar electronic contributions to the bonds, it is expected that the most sterically congested complex will have the weakest bond.

Solution values for the *first* Ni–P bond dissociation enthalpies of several NiL_4 complexes were measured by Tolman's group [141,142] through equilibrium studies at several temperatures. It is noted that these values are substantially lower than $\bar{D}$(Ni–P) for NiL_3 and NiL_4 complexes.

The first Ni–P bond dissociation enthalpy in $Ni[P(O\text{–}o\text{-Tol})_3]_4$ was also reported by McKinney and Roe [143]. The value obtained (71 ± 2 kJ mol^{-1}) is 17 kJ mol^{-1} higher than the one given by Tolman, but still well below $\bar{D}$(Ni–P). McKinney and Roe have also determined the enthalpy change associated with replacing one $P(O\text{–}o\text{-Tol})_3$ in $Ni[P(O\text{–}o\text{-Tol})_3]_4$ by ethylene (Table 7), which reflects the difference $D(Ni\text{–}P) - D(Ni\text{–}C_2H_4) = -17 \pm 4$ kJ mol^{-1} and allows $D(Ni\text{–}C_2H_4)$ to be calculated as 88 kJ mol^{-1}. Also interesting is the comparison of $D[Ni\text{–}P(O\text{–}o\text{-Tol})_3]$ values in $Ni[P(O\text{–}o\text{-Tol})_3]_4$ (71 ± 2 kJ mol^{-1}) and in $Ni[P(O\text{–}o\text{-Tol})_3]_3(C_2H_4)$ (53 ± 4 kJ mol^{-1}), also shown in Table 7. Although these values have been obtained from van't Hoff plots over different temperature ranges [143], their difference is such as to indicate that the ethylene weakens the Ni–P bond. It is finally noted that the difference $D[Ni\text{–}P(O\text{–}o\text{-Tol})_3] - D(Ni\text{–}C_2H_4) = -14$ kJ mol^{-1} [144] for the complexes $Ni[P(O\text{–}o\text{-Tol})_3]_3$ and $Ni[P(O\text{–}o\text{-Tol})_3]_2(C_2H_4)$ compares with the same difference for the complexes $Ni[P(O\text{–}o\text{-Tol})_3]_4$ and $Ni[P(O\text{–}o\text{-Tol})_3]_3(C_2H_4)$ (−17 kJ mol^{-1}).

Information on the difference between $\bar{D}[Ni\text{–}P(O\text{–}p\text{-Tol})_3]$ or $\bar{D}[Ni\text{–}P(O\text{–}p\text{-}C_6H_4Cl)_3]$ and D(Ni–L) is obtained from Tolman's equilibrium studies in benzene involving the complexes $Ni(PR_3)_3$, where $PR_3 = P(O\text{–}p\text{-Tol})_3$ or $P(O\text{–}p\text{-}C_6H_4Cl)_3$, and several olefins [145] (Table 7). The aim of these results was, however, to probe the influence of the phosphite on D(Ni–L). No absolute values of $\bar{D}$(Ni–P) can be derived.

The enthalpies of the reactions of $[Ni(\eta^3\text{-}MeC_3H_3Me)]_2(\mu\text{-}Me)_2$ with a variety of phosphines and phosphites were measured by Schenkluhn et al. [146]. Although the results presented in Table 7 do not allow one to calculate absolute values of D(Ni–P), they yield a relative trend ($L7 = D(Ni\text{–}PMe_3)$). A correlation of the reaction enthalpies with steric and electronic parameters of the phosphorus ligands was presented by the authors. The exothermicity of the reaction increases with the acidity of L and decreases for bulky ligands.

Partenheimer measured the enthalpies of a series of reactions of $Pd(Cl)_2(PhCN)_2$ with olefins, aiming to derive a relative trend of D(Pd–olefin) [147]. One of the values refers, however, to the reaction with diphos, yielding $\bar{D}(Pd\text{–}NCPh) - D(Pd\text{–}diphos) = 211 \pm 7$ kJ mol^{-1}. Partenheimer and Hoy examined the reaction of the same complex with PPh_3 [138], which affords

$\bar{D}$(Pd–NCPh) – $\bar{D}$(Pd–PPh_3) = 82 ± 5 kJ mol^{-1}. These two values lead to D(Pd–diphos)/2 – $\bar{D}$(Pd–PPh_3) = 24 ± 4 kJ mol^{-1}, which is in the same range as the value observed for the molybdenum tetracarbonyl complexes, 16 kJ mol^{-1}. The same authors measured the enthalpy of the reaction of $Pd(Cl)_2(cod)$ with $P(OPh)_3$, yielding D(Pd–cod) – $2\bar{D}$[Pd–$P(OPh)_3$] = –89 ± 2 kJ mol^{-1}. This value is close to $\bar{D}$(Ni–cod) – $2\bar{D}$[Ni–$P(OPh)_3$] = –82 ± 2 kJ mol^{-1}, i.e. one half of the enthalpy of reaction between $Ni(cod)_2$ and $P(OPh)_3$ (Table 7).

The enthalpy of the last reaction for palladium listed in Table 7 is a direct measurement of Pd–PPh_3 bond dissociation enthalpy in the complex *trans*-$Pd(PPh_3)_2(Cl)(COCOPh)$ [148]. A van't Hoff plot was also the source of the first Pt–PCy_3 bond dissociation enthalpy in $Pt(PCy_3)_3$, 55 ± 2 kJ mol^{-1} [56], shown in Table 7.

Calorimetric studies by Partenheimer led to the enthalpy of ethylene displacement by triphenylphosphite in $Pt(Cl)_2(py)(C_2H_4)$ [149]. The enthalpy of reaction of the product complex $Pt(Cl)_2(py)[P(OPh)_3]$ with another $P(OPh)_3$ molecule, giving $Pt(Cl)_2[P(OPh)_3]_2$, was also measured. These results, presented in Table 7, lead to D(Pt–C_2H_4) – D[Pt–$P(OPh)_3$] = –58 kJ mol^{-1} and to D(Pt–py) – D[Pt–$P(OPh)_3$] = –44 kJ mol^{-1}, respectively.

The last series of reaction enthalpies involving platinum complexes in Table 7, measured by Manzer and Tolman, do not allow one to derive the absolute values of D(Pt–P), but yield their trend [150].

Group 11. Partenheimer and Johnson reported the enthalpy of replacement of cyclooctadiene in Ag(hfacac)(cod) by triphenylphosphine as –49.0 ± 0.8 kJ mol^{-1}, which reflects D(Ag–cod) – D(Ag–PPh_3) [151]. The last enthalpy of reaction in Table 7, measured by the same authors, is identified with the first Ag–PPh_3 bond dissociation enthalpy in $Ag(hfacac)(PPh_3)_2$.

4.2.2 Enthalpy of formation data

The available standard enthalpies of formation of organometallic complexes containing phosphorus ligands, together with the enthalpies of sublimation of some compounds for which no enthalpy of formation data are known, are presented in Table 8 [152–163]. Also included in the table are the calculated values of metal–phosphorus bond dissociation enthalpies or mean bond dissociation enthalpies.

Group 4. The enthalpies of formation of the bis(cyclopentadienyl) titanium complexes shown in Table 8 were determined from the enthalpies of their reactions with iodine [152]:

$$Ti(Cp)_2(PR_3)_2(c) + I_2(c) = Ti(Cp)_2I_2(c) + 2PR_3(l) \quad (28)$$

$$\Delta H = -144.7 \pm 5.5 \text{ kJ mol}^{-1}$$

$$Ti(Cp)_2(CO)PR_3(c) + I_2(c) = Ti(Cp)_2I_2(c) + CO(g) + PR_3(l) \quad (29)$$

TABLE 8

Standard enthalpies of formation of transition metal complexes containing metal–phosphorus(III) ligands
Data in kJ mol^{-1}

Complex	Method/Ref.[a]	ΔH_f^0(c)	$\Delta H_{s/v}^0$ [b]	ΔH_f^0(g)	D(M–P)[c]
$Ti(Cp)_2(PMe_3)_2$,c	RSC/152	-262 ± 17^d	(90 ± 10)	-172 ± 20^d	159 ± 8^e
$Ti(Cp)_2(CO)(PMe_3)$,c	RSC/152	-285 ± 17^d	(90 ± 10)	-195 ± 19^d	L10[f]
$Ti(Cp)_2(CO)(PEt_3)$,c	RSC/152	-303 ± 19^d	(100 ± 10)	-203 ± 21^d	L10 − (2 ± 11)[f]
$Cr(CO)_5PMe_3$,c	160		91.2 ± 1.6		
$Cr(CO)_5PPh_3$,c	160		170.2 ± 6.8		
$Cr(CO)_5PF_3$,c	161		85.5 ± 2.9		
$Cr(CO)_5PCl_3$,c	161		78.9 ± 1.8		
$Cr(CO)_5PBr_3$,c	161		79.9 ± 1.9		
$Cr(PF_3)_6$,c	CMC/162	-6052 ± 17	(63 ± 8)	-5989 ± 19	107 ± 3
$Mo(CO)_5PCl_3$,c	161		79.3 ± 1.1		
$W(CO)_5PMe_3$,c	160		93.8 ± 1.5		
$W(CO)_5PPh_3$,c	CMC/163	-719 ± 7	144 ± 3	-575 ± 8	319 ± 16^g
$W(CO)_5P(OPh)_3$,c	160		120.2 ± 6.6		
$W(CO)_5PF_3$,c	161		77.4 ± 1.5		
$W(CO)_5PCl_3$,c	161		86.2 ± 1.7		
$W(CO)_5PBr_3$,c	161		77.2 ± 5.3		
$Ni(PF_3)_4$,l	CMC/162	-4025 ± 12	34.6 ± 0.2	-3990 ± 12	147 ± 3
cis-$Pd(PPh_3)_2Cl_2$,c	CMC/106	226 ± 16	(285 ± 20)	511 ± 25	133
cis-$Pt(PEt_3)_2Me_2$,c	CMC/106	-520 ± 6	131 ± 6	-389 ± 8	
cis-$Pt(PEt_3)_2(Cl)Me$,c	CMC/106	-569 ± 5	(152 ± 20)	-417 ± 21	
cis-$Pt(PEt_3)_2$(*o*-Tol)$_2$,c	CMC/106	-329 ± 24	183 ± 4	-146 ± 24	
cis-$Pt(PEt_3)_2(Cl)$(*o*-Tol),c	CMC/106	-495 ± 15	(179 ± 20)	-316 ± 25	
cis-$Pt(PEt_3)_2(SEt)_2$,c	CMC/106	-651 ± 9	196 ± 11	-455 ± 14	
cis-$Pt(PEt_3)_2Cl_2$,c	CMC/106	-655 ± 15	174 ± 16	-481 ± 21	188
trans-$Pt(PEt_3)_2Cl_2$,c	CMC/106	-644 ± 7	149 ± 3	-495 ± 8	195
cis-$Pt(PEt_3)_2Cl_4$,c	CMC/106	-863 ± 7	(200 ± 20)	-663 ± 21	
trans-$Pt[P(i\text{-}Pr)_3]_2Cl_2$,c	CMC/106	-785 ± 7	193 ± 4	-592 ± 8	204

trans-$Pt(PPh_3)_2(H)Cl$,c	RSC/159	289 ± 27	(245 ± 20)	534 ± 34	
$Pt(PPh_3)_2(CPhCHPh)Cl$,c	RSC/159	571 ± 20			
cis-$Pt(PPh_3)_2(Me)I$,c	RSC/159	361 ± 23	(264 ± 20)	625 ± 31	
cis-$Pt(PPh_3)_2(SEt)_2$,c	CMC/106	203 ± 15	(295 ± 20)	498 ± 25	
$Pt(PPh_3)_2(C_2H_4)$,c	RSC/159	477 ± 23	(230 ± 20)	707 ± 31	
$Pt(PPh_3)_2(PhCHCH_2)$,c	RSC/159	530 ± 23	(255)	785 ± 30	
$Pt(PPh_3)_2(C_2Ph_2)$,c	RSC/159	753 ± 19	(285 ± 20)	1038 ± 28	
$Pt(PPh_3)_2$(*cis*-$C_2H_2Ph_2$),c	RSC/159	585 ± 23	(280)	865 ± 30	
$Pt(PPh_3)_2$(*trans*-$C_2H_2Ph_2$),c	RSC/159	551 ± 23	(280)	831 ± 30	
$Pt(PPh_3)_2$(dpcb),c	RSC/159	771 ± 24	(288 ± 20)	1059 ± 31	
$Pt(PPh_3)_2[C_2(CN)_4]$,c	RSC/159	975 ± 25	(260 ± 20)	1235 ± 32	
$Pt(PPh_3)_2(CS_2)$,c	RSC/159	498 ± 23	(245 ± 20)	743 ± 31	
cis-$Pt(PPh_3)_2Cl_2$,c	CMC/106	194 ± 12	(275 ± 20)	469 ± 23	146 ± 13
cis-$Pt(PPh_3)_2I_2$,c	RSC/159	328 ± 23	(304 ± 15)	632 ± 28	
trans-$Pt(PPh_3)_2I_2$,c	RSC/159	311 ± 24			
trans-$Pt(PCy_3)_2Cl_2$,c	CMC/106	−999 ± 8	(300 ± 20)	−699 ± 21	200
cis-$Pt(PMe_2Ph)_2Cl_2$	CMC/106	−280 ± 5	(185 ± 20)	−95 ± 21	140

[a] CMC = Calvet microcalorimetry; RSC = reaction–solution calorimetry.
[b] Estimated values in parentheses.
[c] Mean bond dissociation enthalpy, unless indicated otherwise.
[d] Provisional values. See text.
[e] Relies on $\bar{D}$(Ti–I) = 294 ± 2 kJ mol^{-1}.
[f] Bond dissociation enthalpy. L10 = *D*(Ti–PMe_3).
[g] Bond dissociation enthalpy.

$\Delta H = -102.7 \pm 9.2$ kJ mol^{-1} (R = Me)

$\Delta H = -104.2 \pm 5.6$ kJ mol^{-1} (R = Et)

The results in Table 8 rely, therefore, on the enthalpy of formation of $Ti(Cp)_2I_2$. This was calculated as -148.3 ± 13.1 kJ mol^{-1} from the enthalpy of reaction (30), also determined from reaction–solution calorimetry experiments [153]:

$$Ti(Cp)_2(CO)_2(c) + I_2(c) = Ti(Cp)_2I_2(c) + 2CO(g) \quad (30)$$

$\Delta H = -74.1 \pm 2.1$ kJ mol^{-1}

The value of $\Delta H_f^0[Ti(Cp)_2I_2,c]$, and hence the enthalpies of formation of the phosphine complexes, are based on $\Delta H_f^0[Ti(Cp)_2(CO)_2,c] = -295.3 \pm 12.9$ kJ mol^{-1} [154]. This value has been recalculated by the same group as -371.5 ± 12.9 kJ mol^{-1} [155], but more recent experimental evidence [156] about the reaction from which $\Delta H_f^0[Ti(Cp)_2(CO)_2,c]$ was derived questions the reliability of those values. Experiments are in progress to settle this problem, but meanwhile the values in Table 8 should be regarded as provisional. The above reaction enthalpies, however, are considered reliable and allow the mean bond dissociation enthalpies shown in Table 8 to be estimated.

Relative gas-phase values of $\bar{D}$(Ti–CO), $\bar{D}$(Ti–PMe$_3$), and $\bar{D}$(Ti–I) can be obtained from the enthalpies of reactions (28) and (30), together with the sublimation enthalpies of the complexes, $D(I–I) = 151.1 \pm 0.1$ kJ mol^{-1}, and the enthalpy of vaporization of PMe$_3$ (Table 6): $\bar{D}$(Ti–I) − $\bar{D}$(Ti–PMe$_3$) = 135 ± 8 kJ mol^{-1}, $\bar{D}$(Ti–I) − $\bar{D}$(Ti–CO) = 126 ± 8 kJ mol^{-1} and $\bar{D}$(Ti–CO) − $\bar{D}$(Ti–PMe$_3$) = 9 ± 6 kJ mol^{-1}. The estimated enthalpies of sublimation of $Ti(Cp)_2I_2$, 120 ± 10 kJ mol^{-1} [153], and $Ti(Cp)_2(PMe_3)_2$, 90 ± 10 kJ mol^{-1}, are thought to be fairly reliable, in particular that for the bis(trimethylphosphine) complex (the experimental value of the enthalpy of sublimation of $Ti(Cp)_2(CO)_2$ is 84.2 ± 3.5 kJ mol^{-1} [153]). The conclusion that $\bar{D}$(Ti–CO) ≈ $\bar{D}$(Ti–PMe$_3$) looks sensible. Note, however, that, for the molybdenum complexes discussed in the previous paragraph, $\bar{D}$(Mo–CO) − $\bar{D}$(Mo–PMe$_3$) is in the range of −10 to −23 kJ mol^{-1}. $\bar{D}$(Ni–CO) − $\bar{D}$(Ni–PMe$_3$), in Ni(PMe$_3$)$_4$ and Ni(CO)$_4$, on the other hand, is 5 kJ mol^{-1} ($\bar{D}$(Ni–PMe$_3$) was taken from Table 7 and $\bar{D}$(Ni–CO) = 147 ± 1 kJ mol^{-1} was calculated from the enthalpy of formation given in ref. 110. As stressed before, it is hardly possible to extract many meaningful conclusions from these comparisons between gas-phase and solution data, except that the bonding energetics of M–CO and M–PMe$_3$ are similar.

It is interesting to compare the enthalpy of reaction (29) for R = Me with the enthalpies of reactions (28) and (30). It is noted that $[\Delta H(28) + \Delta H(30)]/2 = -109.4 \pm 2.9$ kJ mol^{-1} is close to $\Delta H(29)$, meaning that reaction (31) is approximately thermoneutral: $\Delta H(31) = -13.4 \pm 19.3$ kJ mol^{-1}.

$$Ti(Cp)_2(CO)_2(c) + Ti(Cp)_2(PMe_3)_2(c) = 2Ti(Cp)_2(CO)PMe_3(c) \quad (31)$$

In other words, as it is very likely that the enthalpy of this reaction in the gas phase is also about -13 kJ mol^{-1}, the Ti–CO and/or Ti–PMe$_3$ bonds are only slightly strengthened in the mixed complex.

A comparison between the enthalpies of reaction (29) for R = Me and R = Et leads to $D(\text{Ti–PMe}_3) - D(\text{Ti–PEt}_3) = 1.5 \pm 10.8$ kJ mol^{-1}. As above, it was assumed that the enthalpy of reaction (32) is the same in the gas phase.

$$\text{Ti(Cp)}_2\text{(CO)PMe}_3\text{(c)} + \text{PEt}_3\text{(l)} = \text{Ti(Cp)}_2\text{(CO)PEt}_3\text{(c)} + \text{PMe}_3\text{(l)} \quad (32)$$

The "absolute" value of the Ti–PMe$_3$ mean bond dissociation enthalpy shown in Table 7 relies on $\bar{D}(\text{Ti–I}) = 294 \pm 2$ kJ mol^{-1}, the mean bond dissociation enthalpy in TiI$_4$ [157,140], which was therefore identified with $\bar{D}$(Ti–I) in Ti(Cp)$_2$I$_2$.

Group 6. The chromium–trifluorophosphine mean bond dissociation enthalpy in Cr(PF$_3$)$_6$ was evaluated as 107 ± 3 kJ mol^{-1} (Table 8), matching the value of $\bar{D}$(Cr–CO) in Cr(CO)$_6$, 107 ± 1 kJ mol^{-1} [110].

The tungsten–triphenylphosphine bond dissociation enthalpy in W(CO)$_5$PPh$_3$, 319 ± 16 kJ mol^{-1}, is presented in Table 8 and was derived from the enthalpy of formation of this molecule, $\Delta H_f^0[\text{W(CO)}_5\text{,g}] = -581 \pm 13$ kJ mol^{-1} [110,121], and ΔH_f^0(PPh$_3$,g) (Table 6). It is noted that $D(\text{W–PPh}_3) - D(\text{W–CO}) = 126$ kJ mol^{-1} is one order of magnitude greater than $D(\text{Mo–PPh}_3) - D(\text{Mo–CO}) = 5$ kJ mol^{-1} in the complexes Mo(Cp)(CO)$_2$(PPh$_3$)H and Mo(Cp)(CO)$_3$H; $\bar{D}(\text{Mo–PPh}_3) - \bar{D}(\text{Mo–CO})$ values, on the other hand, are in the range of -4 to -12 kJ mol^{-1} for several molybdenum compounds shown in Table 7.

Group 10. The enthalpy of formation of gaseous Ni(PF$_3$)$_4$ leads to the value of $\bar{D}(\text{Ni–PF}_3) = 147 \pm 3$ kJ mol^{-1}, which is in the same range as the data presented in Table 7 for Ni(PR$_3$)$_4$ and Ni[P(OR)$_3$]$_4$. The value of $\bar{D}$(Ni–CO) in nickel tetracarbonyl is also 147 ± 1 kJ mol^{-1} [110].

The palladium–triphenylphosphine mean bond dissociation enthalpy in the complex *cis*-Pd(PPh$_3$)$_2$Cl$_2$ (133 kJ mol^{-1}) was calculated from the enthalpy of reaction (33) obtained from the enthalpy of formation in Table 8 and $\Delta H_f^0(\text{PdCl}_2\text{,g}) =$ 128 kJ mol^{-1}. This value is an estimate by Skinner and co-workers [106] and is based on $\Delta H_f^0(\text{PdCl}_2\text{,c}) = -163 \pm 8$ kJ mol^{-1} [158].

$$cis\text{-Pd(PPh}_3)_2\text{Cl}_2\text{(g)} = \text{PdCl}_2\text{(g)} + 2\text{PPh}_3\text{(g)} \quad (33)$$

The enthalpies of formation of a number of complexes of the type Pt(PR$_3$)$_2$L$_2$ are presented in Table 8. They were all derived from Calvet microcalorimetry and reaction–solution calorimetry studies. The Calvet experiments by Skinner and co-workers [106] afforded $\Delta H_f^0[\text{Pt(PPh}_3)_2\text{Cl}_2\text{,c}] = 194 \pm 12$ kJ mol^{-1}. This value was then used as an anchor to calculate the enthalpies of formation of several other triphenylphosphine platinum complexes for which reaction–solution calorimetry data were available. The exercise was made by Mortimer [159], and the values are displayed in Table 8. As stated before, changes in those values reflect different auxiliary data used. The large uncertainties assigned to the enthalpies of formation of the crystalline complexes $Pt(PPh_3)_2L_2$ result from the uncertainty in the enthalpy of formation of the anchor complex. The errors in the gas-phase data, on the other hand, also result from the uncertainties assigned to the estimated enthalpies of sublimation.

Platinum–phosphine mean bond dissociation enthalpies in Table 8 were derived as described for the palladium complex, i.e. by calculating the enthalpies of reaction (34). $\Delta H_f^0(PtCl_2,g)$ was taken as 111 ± 10 kJ mol^{-1}, along with Skinner and co-workers [106].

$$Pt(PR_3)_2Cl_2(g) = PtCl_2(g) + 2PR_3(g) \tag{34}$$

The enthalpies of formation of the gaseous phosphines PEt_3, $P(i\text{-}Pr)_3$, PCy_3, and $PPhMe_2$, respectively -108, -148, -205, and 37 kJ mol^{-1}, were also estimated in ref. 106. The large (mostly unknown) uncertainties that affect $\bar{D}$(Pt–P) in Table 8 hinder a detailed discussion of their trend. However, the large destabilizing effect of the phenyl groups in the phosphine is apparent.

4.2.3 General discussion of thermochemical data

It is apparent from Tables 7 and 8 that most studies (about 80%) on the energetics of the metal–phosphorus(III) bond have been devoted to Group 6 and Group 10 transition metals. The great majority of the available data refers to enthalpies of reaction in solution, from which solution-phase bond dissociation enthalpies have been derived (Table 7). These may not be comparable with gas-phase bond dissociation enthalpies (Table 8) due to solvation effects, particularly when coordinatively unsaturated species are involved [122].

Despite the paucity of data, significant efforts have been made to disclose and interpret trends in the energetics of the transition metal–phosphorus(III) bond, particularly by the analysis of the PR_3 or $P(OR)_3$ ligand effects on those bonds. Tolman found that the enthalpies of reactions, ΔH_r, involving the cleavage or formation of M–P bonds in Ni(0) or Pt(II) complexes, could be correlated with the steric (cone angle, θ; see Sect. 3.1 and Table 1) or electronic (ν, χ; see Sect. 3.2.2 and Tables 4 and 5) properties of the phosphorus(III) ligands (eqn. (35)) [46(b),139,141,142,144,145,150].

$$\Delta H_r = a\theta + b\nu + c \tag{35}$$

While fair correlations can be obtained by applying eqn. (35) to different reactions, large deviations are observed, and Tolman's equation cannot be regarded as a reliable method for the estimation of ΔH_r. For example, multilinear regression analysis of the enthalpies of the reaction

$$[\textit{trans}\text{-}Pt(PPhMe_2)_2(Me)(thf)]PF_6(soln) + L(soln)$$
$$= [\textit{cis/trans}\text{-}Pt(PPhMe_2)_2(Me)(L)]PF_6(soln) + thf(soln) \tag{36}$$

($L = PR_3$ or $P(OR)_3$, Table 7) as a function of Tolman's θ (Table 1) and ν ($\nu/\text{cm}^{-1} = 2056.1 + {}^{FT}\chi$; Table 5) parameters gives eqn. (37) ($r = 0.87$). The average deviation of the enthalpies of reaction estimated by eqn. (37) from the experimental values is ca. 15 kJ mol^{-1}, but deviations up to ca. 35 kJ mol^{-1}, as in the case of $L = (P\text{—}o\text{-Tol})_3$, are obtained.

$$-\Delta H_r(36)/(\text{kJ mol}^{-1}) = -(1.0523 \pm 0.1543)\theta - (0.2870 \pm 0.4030)\nu - 826.3 \pm 15.8 \tag{37}$$

Giering and co-workers have discussed the enthalpies of a series of reactions, including reaction (36), by using a method called "quantitative analysis of ligand effects" (QALE) [17,44]. The main assumptions are summarized below and the application of the method is illustrated for reaction (36) [44(b)]. The QALE method is still under development and the changes introduced in recent versions will be discussed later. (1) It is assumed that the M—P interaction includes contributions from σ and π electronic effects, as well as σ and π steric effects. (2) The σ electronic contribution is measured by the pK_a of PR_3H^+ [44(b)]. (3) Steric ligand effects are represented by Tolman's cone angle, θ. It is observed that the onset of steric effects occurs abruptly when the size of the ligand exceeds a given value, θ_{st} (steric threshold). (4) A critical point of the QALE analysis is the classification of ligands into classes based on their electronic character. Initially [44(b)] three classes of ligand were introduced: σ donor/π donor (class I), σ donor (class II), and σ donor/π acceptor (class III). These classes were defined, to a first approximation, from the analysis of the correlations of formal reduction potentials, $E°$, for $Mn(MeCp)(CO)_2L$ (L = phosphine or phosphite) complexes with the pK_a of LH^+ [44(a),44(b)]. In the case of class II (σ donor) ligands, $E°$ is linearly related to pK_a. Complexes containing class III ligands (π acids) are more difficult to oxidize than predicted by the correlation, whereas those containing class I ligands (π bases) have lower oxidation potentials than predicted by the correlation. The deviations observed for class III and class I ligands, $E_{\pi a}$ and $E_{\pi b}$, respectively, (Table 9) are used as measures of the π interaction in the M—P bond. A π electronic threshold, π_t, is observed and assigned to the onset of phosphorus–metal π bonding. (5) The enthalpies of reaction (ΔH_r) can be decomposed into four contributions (eqn. (38)): σ electronic (ΔH_σ), σ steric (ΔH_σ^{st}), π electronic (ΔH_π), and π steric (ΔH_π^{st}).

$$\Delta H_r = \Delta H_\sigma + \Delta H_\sigma^{st} + \Delta H_\pi + \Delta H_\pi^{st} \tag{38}$$

(6) The σ electronic contribution is a linear function of the pK_a values of the protonated ligands before and after the steric threshold (eqn. (39)).

$$-\Delta H_\sigma = a\text{p}K_a + c \tag{39}$$

The pK_a dependence of ΔH_r is considered to be the same for all classes of ligand, regardless of the presence or absence of steric effects. The coefficients a and c in eqn. (39) can therefore be obtained from a linear plot of data for pure σ donor (class II) ligands before the steric threshold. Alternatively, if the data for class II ligands are not sufficient to define a correlation, a is determined by multilinear regression analysis of data for class I or class III ligands before the steric threshold (see below). (7) The π electronic term, ΔH_π, is given by the deviations of class III or class I ligands from eqn. (39) in the absence of steric effects. ΔH_π is linearly related to $E_{\pi a}$ (or $E_{\pi b}$) before and after the steric thresholds (eqn. (40)).

$$-\Delta H_\pi = bE_{\pi a} + c_1 \tag{40}$$

(8) Steric effects generate deviations of class II ligands from the linear relation (39), ΔH_σ^{st} representing these deviations. A linear plot of ΔH_σ^{st} vs. the cone angle θ generates the σ steric profile of the reaction (eqn. (41)).

$$-\Delta H_\sigma^{st} = d\theta + c_2 \tag{41}$$

If steric effects are important for all the class II ligands, the a and d coefficients are derived by multilinear regression analysis of the data (eqn. (42)).

$$-\Delta H_r(\text{class II}) = -\Delta H_\sigma - \Delta H_\sigma^{st} = a\mathrm{p}K_a + d\theta + c_3 \tag{42}$$

$$\Delta H_\pi^{st} = e\theta + c_4 \tag{43}$$

(9) The π steric profile of the reaction (eqn. (43)) is obtained by plotting the deviations, ΔH_π^{st}, of class I or class III ligands from eqn. (40).

Figure 9 represents a plot of the enthalpy of reaction (36) (L = PR_3 or $P(OR)_3$, Table 7) as a function of the pK_a values of LH^+. In this case, only three class II ligands are available for which no steric effects are expected: PMe_3, PPh_2Me, and $PPhMe_2$. The slope, $a = 5.71$, of the line shown was therefore calculated by multilinear regression analysis of data for the five class III ligands with the smallest cone angles (eqn. (44), $r = 0.96$): $P(OCH_2)_3CPr$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, and P(O–i-Pr)$_3$).

$$-\Delta H_r(36)/(\mathrm{kJ\ mol^{-1}}) = 5.71\mathrm{p}K_a + 162.88E_{\pi a} + 60.71 \tag{44}$$

While not explicitly indicated in their paper [44(b)], Giering and co-workers have assumed that the pK_a and $E_{\pi a}$ of $P(OCH_2)_3CPr$ were the same as for $P(OCH_2)_3CEt$ (pK_a = 1.74 and $E_{\pi a}$ = 0.25 V). The line in Fig. 9 was adjusted to pass through the data points for PPh_2Me and $PPhMe_2$, which Giering and co-workers found to behave consistently as class II ligands [44(b)]. This leads to an ordinate $c = 66.93$ and therefore the σ electronic profile of reaction (36) is given by eqn. (45).

$$-\Delta H_\sigma(36)/(\mathrm{kJ\ mol^{-1}}) = 5.71\mathrm{p}K_a + 66.93 \tag{45}$$

Class III ligands with cone angles smaller than 170° lie above the line defined by eqn. (45) and class I ligands lie below that line. It should be noted that PMe_3, which is a class II ligand based on the correlations of formal reduction potentials for $Mn(MeCp)(CO)_2L$ (L = phosphine or phosphite) complexes with the pK_a of LH^+,

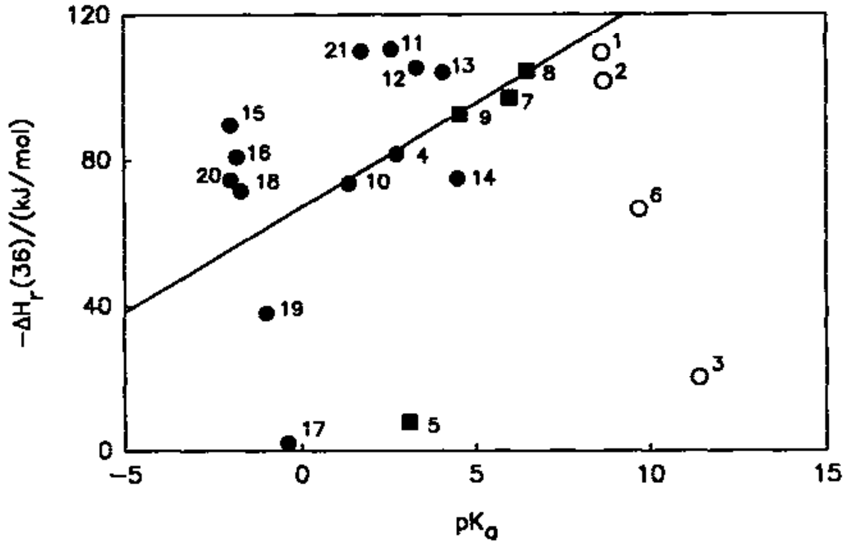

Fig. 9. σ electronic profile of reaction (36) (see text). 1 = PMe_3; 2 = PEt_3; 3 = $P(t\text{-}Bu)_3$; 4 = PPh_3; 5 = $P(o\text{-}Tol)_3$; 6 = PCy_3; 7 = PBz_3; 8 = $PPhMe_2$; 9 = PPh_2Me; 10 = $P(CH_2CH_2CN)_3$; 11 = $P(OMe)_3$; 12 = $P(OEt)_3$; 13 = $P(O\text{–}i\text{-}Pr)_3$; 14 = $P(O\text{–}t\text{-}Bu)_3$; 15 = $P(OPh)_3$; 16 = $P(O\text{–}o\text{-}Tol)_3$; 17 = $P(O\text{–}2,6\text{-}C_6H_3Me_2)_3$; 18 = $P(O\text{–}o\text{-}C_6H_4\text{-}i\text{-}Pr)_3$; 19 = $P(O\text{–}o\text{-}C_6H_4\text{–}t\text{-}Bu)_3$; 20 = $P(O\text{–}o\text{-}C_6H_4Ph)_3$; 21 = $P(OCH_2)_3CPr$.

also lies below the line in Fig. 9. Giering and co-workers [44(b)] attributed this deviation to the fact that data for manganese complexes were used in the preliminary definition of the classes and that by changing the metal to Pt(II) the classification of the ligands is affected. According to these authors, PMe_3 should be regarded, in this case, as a class I ligand.

The σ steric profile (Fig. 10) is obtained by plotting the deviations, ΔH_σ^{st}, of bulky class II and class III ligands from the line in Fig. 9 as a function of θ. $\Delta H_\sigma^{st} = 0$ before the steric threshold, which occurs at $\theta \simeq 165°$. After the steric threshold, ΔH_σ^{st} is given by eqn. 46(b).

$$\theta \leqslant 165° \quad -\Delta H_\sigma^{st} = 0 \tag{46a}$$

$$\theta \geqslant 165° \quad -\Delta H_\sigma^{st}/(\text{kJ mol}^{-1}) = -2.515\theta + 413.87 \tag{46b}$$

Figure 11 represents a plot of the deviations of all class III ligands from eqn. (45). The line shown has a slope of 162.88 (see eqn. (44)), and was adjusted to the data for ligands without steric effects ($P(OCH_2)_3CPr$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, and $P(O\text{–}i\text{-}Pr)_3$) to generate the π electronic profile (eqn. (47)).

$$-\Delta H_\pi = 0 \quad E_{\pi a} \leqslant 0.038 \tag{47a}$$

$$-\Delta H_\pi/(\text{kJ mol}^{-1}) = 162.88E_{\pi a} - 6.11 \quad E_{\pi a} > 0.038 \tag{47b}$$

The onset of π electronic effects ($\Delta H_\pi = 0$ kJ mol^{-1}) occurs when $E_{\pi a} = 0.038$ V. The

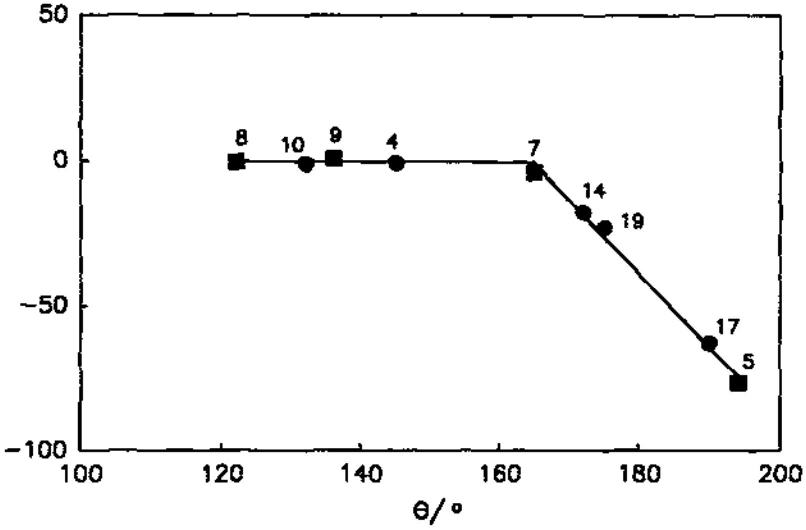

Fig. 10. σ steric profile of reaction (36) (see text and caption of Fig. 9).

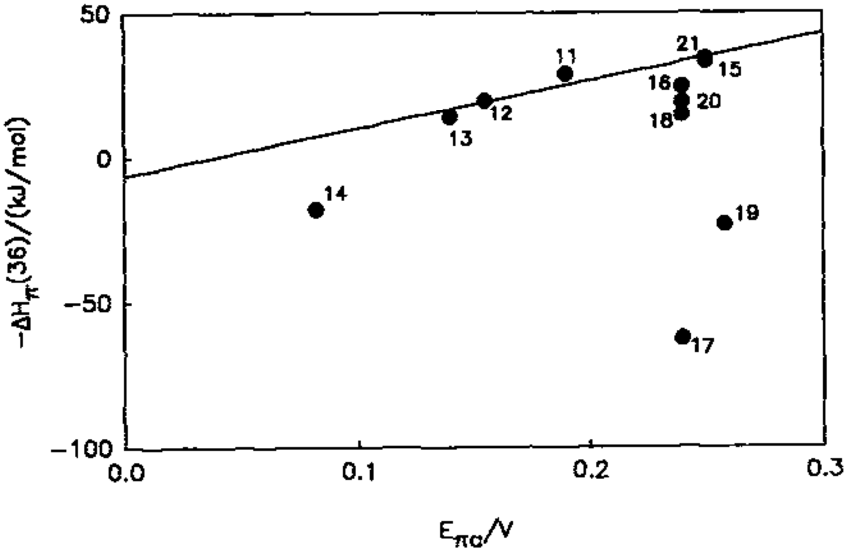

Fig. 11. π electronic profile of reaction (36) (see text and caption of Fig. 9).

π steric profile (Fig. 12) corresponds to a plot of the deviations of large class III ligands from eqn. (47), and is given by eqn. (48). In this case the π steric profile exhibits two steric thresholds, one at $\theta = 130°$ and another at $\theta = 169°$. Equations (45)–(48) can be used to estimate the enthalpies of reaction (36) for class II and class III ligands. Class I phosphines were not considered in the above example because only four of these ligands are present and the $E_{\pi b}$ values needed to determine

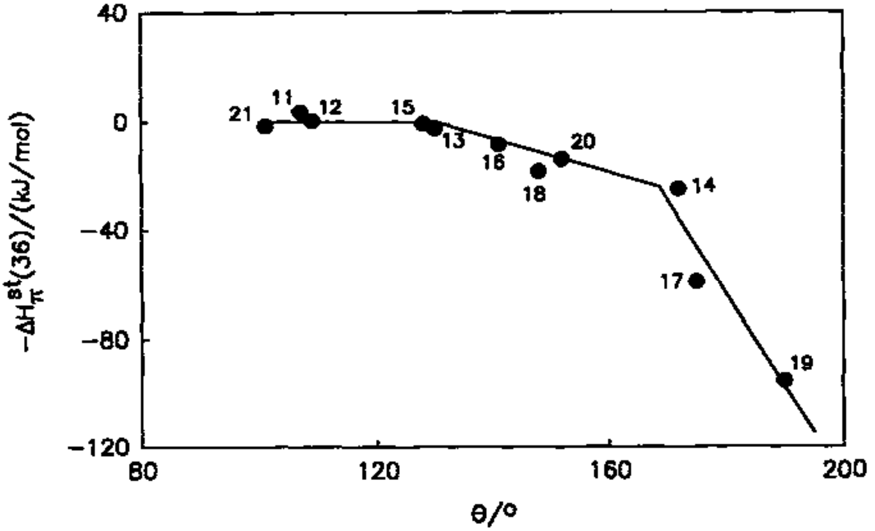

Fig. 12. π steric profile of reaction (36) (see text and caption of Fig. 9).

their π electronic profile are not available for PMe_3 and $P(t\text{-}Bu)_3$ (ref. 44(b) and Table 9).

$$-\Delta H_{\pi}^{st} = 0 \quad \theta \leqslant 130° \tag{48a}$$

$$-\Delta H_{\pi}^{st}/(\text{kJ mol}^{-1}) = -0.52\theta + 64.09 \quad 130° < \theta < 169° \tag{48b}$$

$$-\Delta H_{\pi}^{st}/(\text{kJ mol}^{-1}) = -3.439\theta + 555.79 \quad \theta \geqslant 169° \tag{48c}$$

The QALE method relies on four parameters (ΔH_{σ}, ΔH_{σ}^{st}, ΔH_{π}, and ΔH_{π}^{st}), and it is therefore not surprising that it reproduces the data for reaction (36) much better than eqn. (37). For example, the estimated enthalpy of reaction (36) for $P(o\text{-Tol})_3$ is −10.5 kJ mol^{-1}, which represents a deviation of only 2.6 kJ mol^{-1} relative to the experimental value (−7.9 kJ mol^{-1}; Table 7). This result contrasts with the 35 kJ mol^{-1} deviation obtained by using eqn. (37). The major problem in applying the QALE method to estimate enthalpies of reaction seems to be the definition of a general criteria for classification of ligands into classes. For example, as noted above, the selection based on the correlation of formal reduction potentials for $Mn(MeCp)(CO)_2L$ (L = phosphine or phosphite) complexes with the pK_a of LH^+ indicates that PMe_3 is a class II ligand, but the analysis of reaction (36) suggests that it is a class I ligand. Another relevant aspect is the fact that the existence of class I (σ donor/π donor) phosphines does not seem to conform to the bonding properties of these compounds. These problems were recognized by Giering and co-workers who, in the most recent versions of the QALE method, redefined the criteria for separation of phosphorus(III) ligands into classes [17,44(c)]. This led to the assimilation of class I ligands into class II (pure σ donor). According to the new

TABLE 9

Electronic parameters of the QALE method for phosphorus(III) ligands

Molecule[a]	χ_d[b] (cm^{-1})	$E_{\pi a}$[c] (V)	$E_{\pi b}$[c] (V)
PR_3			
PCl_3	48.00		
PMe_3	8.55		
PEt_3	6.30		0.004
$P(CH_2CH_2CN)_3$	16.79		
$P(i\text{-}Pr)_3$	3.45		
PBu_3	5.25		0.027
$P(i\text{-}Bu)_3$	5.70		
$P(t\text{-}Bu)_3$	0.00		
PCy_3	1.40		0.07
PPh_3	13.25	0.069	
$P(p\text{-}C_6H_4F)_3$	15.70		
$P(p\text{-}C_6H_4Cl)_3$	16.80		
$P(p\text{-}C_6H_4CF_3)_3$	20.2		
$P(o\text{-}Tol)_3$	9.9		
$P(p\text{-}Tol)_3$	11.5		
$P(p\text{-}C_6H_4OMe)_3$	10.50		
$P(p\text{-}C_6H_4NMe_2)_3$	5.25		
PBz_3	10.35		
$P(OMe)_3$	16.70	0.19	
$P(OEt)_3$	15.51	0.155	
$P(O\text{–}i\text{-}Pr)_3$	12.90	0.14	
$P(OBu)_3$	15.2	(0.155)	
$P(O\text{–}t\text{-}Bu)_3$	9.3	0.082	
$P(OPh)_3$	22.05	0.25	
$P(O\text{–}o\text{-}Tol)_3$	20.8	0.24	
$P(O\text{–}o\text{-}C_6H_4\text{–}i\text{-}Pr)_3$	20.1	0.24	
$P(O\text{–}o\text{-}C_6H_4\text{–}t\text{-}Bu)_3$	17.2	0.258	
$P(O\text{–}o\text{-}C_6H_4Ph)_3$	20.21	0.24	
$P(O\text{–}2,6\text{-}C_6H_3Me_2)_3$	15.3	(0.24)	
$P(OMen)_3$	12.7	0.109	
PPh_2R			
PPh_2H	17.35		
PPh_2Cl	24.65		
PPh_2Me	12.10		
PPh_2Et	11.30		
$PPh_2(i\text{-}Pr)$	10.85		
$PPh_2(t\text{-}Bu)$	8.95		
PPh_2Cy	9.40		
PPh_2Bz	12.30		
$PPh_2(OMe)$	14.82	0.11	

TABLE 9 (*continued*)

Molecule[a]	χ_d [b] (cm^{-1})	$E_{\pi a}$ [c] (V)	$E_{\pi b}$ [c] (V)
$PPh_2(OPh)$	9.3	(0.129)	
PPh_2(*o*-C_6H_4OMe)	10.30		
PPhR₂			
$PPhH_2$	20.85		
$PPhCl_2$	36.4		
$PPhMe_2$	10.60		
$PPhEt_2$	9.30		
PPh(*t*-Bu)$_2$	4.95		
$PPhCy_2$	5.55		
$PPh(OMe)_2$	15.73		
$PPh(OEt)_2$	14.98		
$PPh(OPh)_2$	19.1	(0.193)	
$PPh(OMen)_2$	11.8	0.099	
$P(OCH_2)_3CPr$	18.39	0.25	

[a] Bz = benzyl; Cy = cyclohexyl; Tol = tolyl; Men = menthyl.
[b] Data calculated from eqn. (49) (see text and ref. 17).
[c] Data from ref. 44(b). Values in parentheses are estimates.

criteria [44(c)], for complexes containing pure σ donor ligands a plot of the CO stretching frequency (ν_{CO}) as a function of the formal reduction potential, $E°$, gives a straight line, and complexes containing σ donor/π acceptor ligands deviate from this correlation. Note, however, that the need for reference substances is not eliminated by this new rule of selection because, for example, in [*trans*-$Pt(PPhMe_2)_2(Me)(thf)]PF_6$ there are no carbonyl ligands to enable the determination of ν_{CO}. Another modification introduced in the QALE method is the choice of a new parameter, χ_d, to measure the σ donation ability of a ligand (Table 9) [17,44(c)]. χ_d is identified with Tolman's electronic parameter (χ or $^{FT}\chi$) for pure σ donor ligands and is a function of the pK_a of PR_3H^+ and of Tolman's cone angle, θ (eqn. (49)) [17,44(c)].

$$\chi_d/\text{cm}^{-1} = 27.79 - 1.47\text{p}K_a - 0.069\theta \quad (49)$$

According to Giering and co-workers [17,44(c)], χ_d is a better measure of the ligand σ bonding ability than pK_a, because the latter depends on the steric properties of the ligand while the former does not. Figure 13 shows a plot of the enthalpies of reaction (36) as a function of χ_d. The solid line (eqn. (50), $r = 0.88$) was generated by regression of data for all pure σ donor ligands with $\theta < 136°$, for which no steric effects are expected (PMe_3, PEt_3, PPh_3, $PPhMe_2$, PPh_2Me, and $P(CH_2CH_2CN)_3$). Equation (50) reproduces the data for the above ligands with an average deviation

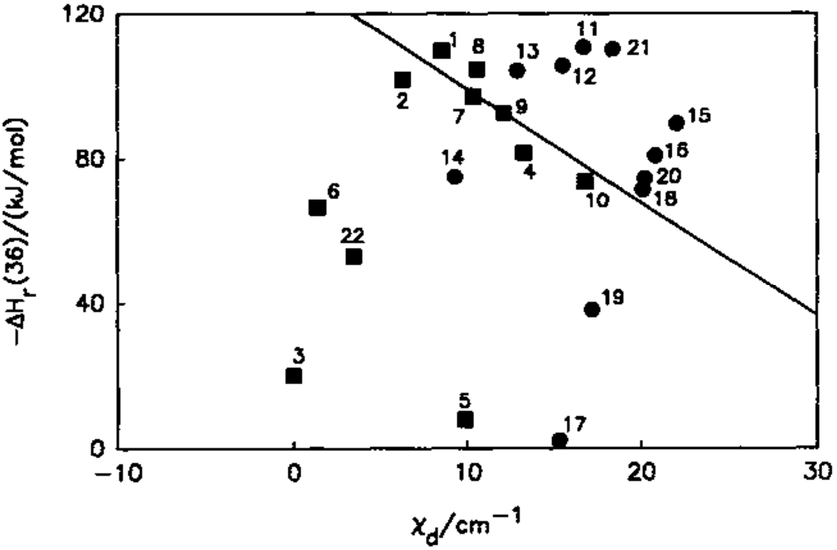

Fig. 13. σ electronic profile of reaction (36) (see text and caption of Fig. 9). 22 = $P(i\text{-}Pr)_3$.

of 6 kJ mol^{-1} and a maximum deviation of 9 kJ mol^{-1} (in the case of PEt_3). If the same set of data is correlated with the pK_a of PR_3H^+ instead of χ_d, eqn. (51) ($r = 0.95$) results.

$$-\Delta H_r/(\mathrm{kJ\ mol^{-1}}) = -3.345\chi_d + 131.6 \tag{50}$$

$$-\Delta H_r/(\mathrm{kJ\ mol^{-1}}) = 4.378\mathrm{p}K_a + 70.2 \tag{51}$$

This equation reproduces the experimental ΔH_r values with an average deviation of 5 kJ mol^{-1} and a maximum deviation of 7 kJ mol^{-1}. Therefore, at least for reaction (36), the introduction of χ_d does not seem to improve the QALE analysis if the goal is estimating enthalpies of reaction. Once the σ electronic profile of the reaction is defined (eqns. (50) or (51)), the calculation of ΔH_σ^{st}, ΔH_π, and ΔH_π^{st} is similar to that presented above for the three-class version of the QALE method.

The bond dissociation enthalpy data in Table 7 show that, in general, for Ti, Mo, and W complexes $D[M\text{–}P(OR)_3] < D(M\text{–}PR_3)$, while for Ni and Pt complexes, $D[M\text{–}P(OR)_3] = D(M\text{–}PR_3)$ (see also Fig. 14). This conclusion does not seem to be significantly affected by the oxidation state of the metal and may reflect the predominance of the σ bonding over the π back-bonding interaction in early transition metal complexes. The above trend is consistent with the decrease of the R–P–R angle and the increase of the P–R bond distance observed by Orpen and co-workers [16(b)] for those complexes and referred in Sect. 2.

It is also indicated by the data in Tables 7 and 8 that $D(M\text{–}PR_3)$ and $D[M\text{–}P(OR)_3]$ decrease along the series R = Me, Et, Bu and that the M–P bond dissociation enthalpies increase on descending a metal group.

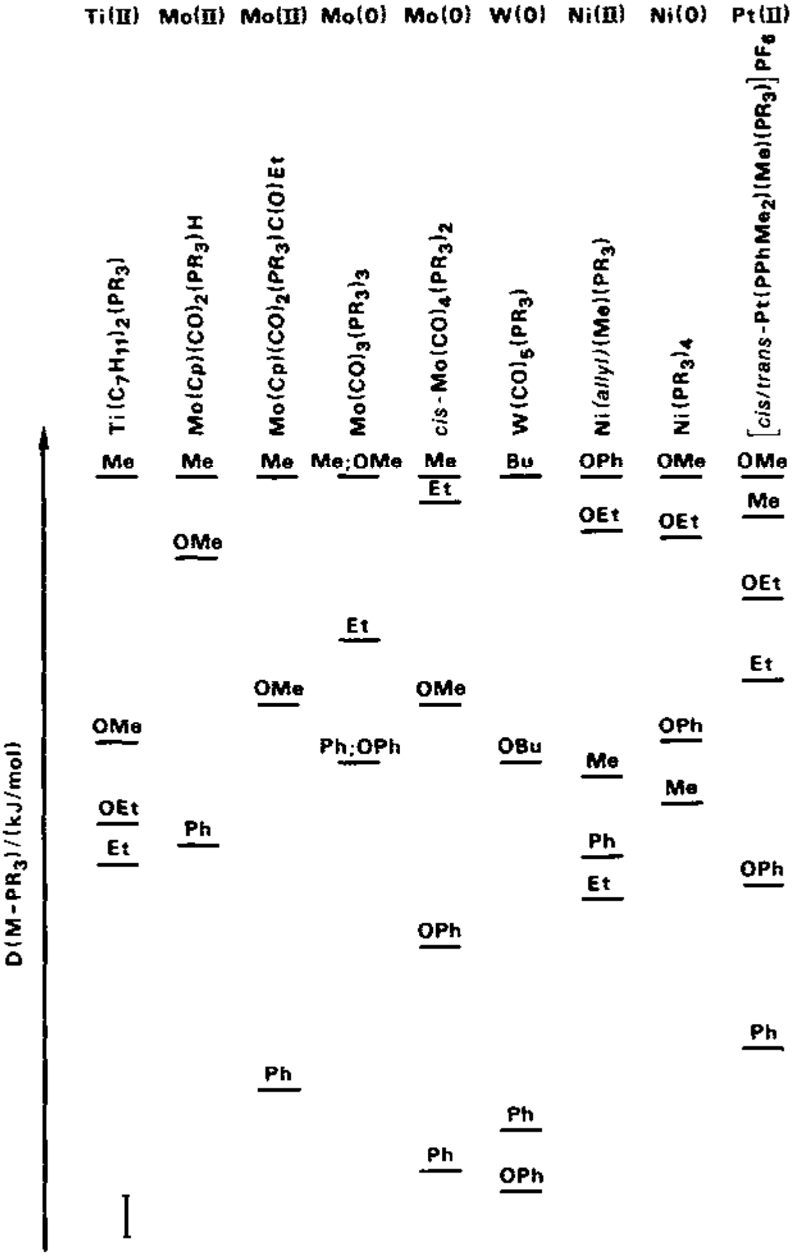

Fig. 14. Trends of several metal–phosphine and metal–phosphite bond dissociation enthalpies. An arbitrary value was assigned to the highest value for each family so that comparisons between two series of complexes cannot be made in the figure. The bar at the bottom represents 2 kJ mol^{-1} for the tungsten family and 1 kJ mol^{-1} for all the others.

As mentioned at the beginning of Sect. 4, the effect of the nature of the phosphine or phosphite on the energetics of other metal–ligand bonds is only briefly covered in the present review. The available information on this important topic is scarce: for example, there are very few studies where the systematics of metal–hydrogen or metal–carbon bond dissociation enthalpies have been examined for a series of phosphorus(III) ligands. In the case of metal–carbon σ bonds, most of the available data has been collected elsewhere [117], including a set of interesting results by Geno and Halpern [164] who measured the activation enthalpies for Co–C homolysis in complexes $Co(dmg)_2(L)Bz$ and $Co(oep)(L)Bz$ (Hdmg = dimethylglyoxime; oep = octaethylporphyrin; L = PBu_3, PPh_3, PCy_3, PMe_2Ph, and PPh_2Et). Under the assumption that the activation enthalpies for the radical recombination reactions are small (ca. 8 kJ mol^{-1}), the authors derived the Co–Bz bond dissociation enthalpy for each case and plotted these data against Tolman's cone angles and the pK_a values for the phosphines. In the case of the dimethylglyoxime complexes, an approximate linear decrease of D(Co–Bz) with θ was observed, but no correlation with pK_a was apparent. By contrast, the linear correlation involving the data for the octaethylporphyrin complexes was only observed by plotting D(Co–Bz) against pK_a. The steric congestion in $Co(dmg)_2(L)Bz$ complexes is probably responsible for the fact that D(Co–Bz) values are determined by the bulkiness of the phosphine, whereas in the less sterically congested Co(oep)(L)Bz complexes, they depend mainly on the basicity of the phosphines (higher pK_a values correspond to stronger cobalt–carbon bonds).

Most of the available examples regarding the influence of phosphorus ligands on metal–hydrogen bond dissociation enthalpies have also been collected elsewhere [117], and many involve Vaska-type complexes, $Ir(X)(CO)(L)_2H_2$ (X = Cl, Br, I; L = phosphine or phosphite). The main conclusion obtained from the data is that the nature of the phosphine or phosphite seems to have a small effect on iridium–hydrogen mean bond dissociation enthalpy. For example, in the series of complexes with X = Cl and L = $P(i\text{-}Pr)_3$, PPh_3, PCy_3, PBz_3, $P(Tol)_3$, PPh_2Bu, and $P(OPh)_3$, $\bar{D}$(Ir–H) varies in the range 240–251 kJ mol^{-1}. A similar conclusion is drawn from a recent study by Tilset and Parker [165], who used an electrochemical method to investigate the energetics of metal–hydrogen bonds in several Cr, Mo, W, Mn, Re, Fe, Ru, and Co carbonyl complexes. In the compounds $Co(CO)_3(L)H$, for example, D(Co–H) is 278, 272, and 273 kJ mol^{-1}, respectively, for L = CO, PPh_3, and $P(OPh)_3$. The approximate constancy of metal–hydrogen bond dissociation enthalpies is also supported by reaction–solution calorimetry results by Hoff and co-workers [166]: in the series of complexes $Cr(Cp)(CO)_2(L)H$, D(Cr–H) is 257, 250, 251, and 262 kJ mol^{-1}, respectively, for L = CO, PPh_3, PEt_3, and $P(OMe)_3$.

Angelici and co-workers [167] observed that the enthalpies of protonation of $Ir(Cp)(CO)PR_3$ and $Fe(CO)_3(PR_3)_2$ (PR_3 = phosphine) complexes in 1,2-dichloroethane become more exothermic as the basicity of the phosphine increases. In the case of the Fe complexes, for example, the enthalpy of protonation changes by

-38 kJ mol^{-1} when PPh$_3$ (p$K_a = 2.73$) is replaced by PMe$_3$ (p$K_a = 8.65$). This trend corresponds to an increase in the basicity of the metal in these complexes with the increase of the phosphine basicity. In contrast, the enthalpies of protonation of $Fe(CO)_3[Ph_2P(CH_2)_nPPh_2]$ ($n = 1$–4) complexes in 1,2-dichloroethane become less exothermic by about 16 kJ mol^{-1} when the chelate ring size increases from $n = 1$ to 4, which corresponds to an increase of the phosphine basicity [168]. The reversed trend observed for the bidentate phosphines was attributed by the authors to the distortions associated to the formation of the chelate ring.

The effect of the nature of the phosphorus ligands on the energetics of other bonds, such as metal–metal, metal–halogen, metal–oxygen, and metal–acyl, can also be found in the literature [169,170]. Whenever possible, these data have been rationalized on the basis of electronic and steric properties of the phosphorus ligands by using methods similar to those described in the present survey.

5. ADDENDUM

Some relevant articles came to our attention after this review had been submitted. Ab initio molecular orbital calculations using model compounds of the type Pd(PX$_3$), Pd(L)(PX$_3$), and Pd(CO)$_3$(PX$_3$) (L = CO or NH$_3$; X = H, F, Me, and OMe) [171] indicate that all the phosphine ligands considered are good σ donors, with PF$_3$ being a moderately weaker base than PMe$_3$. This suggests that the pK_a and the proton affinity are not reliable measures of the σ basicity in zero-valent transition metal complexes. In contrast to the small variation in σ basicity, the π acidity increases markedly along the series $PMe_3 < PH_3 < P(OMe)_3 < PF_3$. The authors also conclude that the phosphorus 3d orbitals are not directly involved in the charge transfer from the metal. They are, however, essential for the correct description of the M–P bond, combining with the P–X σ^* orbitals to form hybridized orbitals which are better suited for π back-bonding than the P–X σ^* orbitals alone. For example, the π acidity of PH$_3$ and PMe$_3$ is considerably reduced when the phosphorus d orbitals are neglected in the calculations. This conclusion is in keeping with the results of previous theoretical studies [6,7].

Although we have not tried to make a comprehensive review of the methods of estimating the steric requirements of ligands, it is worth mentioning that the so-called "ligand repulsive energy parameter", E_R, was recently introduced as a new measure of the steric demands of ligands [172]. Values of E_R have been tabulated for a considerable number of phosphines and phosphites [172]. The E_R values correlate moderately well with Tolman's cone angle.

Reaction–solution calorimetric data for reactions involving the replacement of benzene in M(C$_6$H$_6$)(CO)$_3$ complexes (M = Cr, Mo, and W), by a series of phosphines and phosphites show, as expected, an increase in D(M–P) on descending a transition metal group [173].

Finally, the reactions in thf

$$\mathrm{Fe(BDA)(CO)_3(soln) + 2L(soln) = \mathit{trans}\text{-}Fe(CO)_3L_2(soln) + BDA(soln)}$$

(BDA = benzylideneacetone; L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, PBu_3, and PEt_3) have been studied by reaction–solution calorimetry [174]. The measured enthalpies give a good linear correlation with the carbonyl stretching frequencies in the *trans*-$Fe(CO)_3L_2$ complexes (more exothermic reactions correspond to smaller ν_{CO}). As those reaction enthalpies reflect the difference $D(\mathrm{Fe{-}BDA}) - 2\bar{D}(\mathrm{Fe{-}L})$, the observed correlation indicates that the Fe–phosphorus bond dissociation enthalpies increase with the basicity of the phosphine.

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APPENDIX. AUXILIARY THERMOMECHANICAL DATA

Compound	ΔH_f^0(c/l/g) (kJ mol^{-1})	Ref.
CO_2, g	-393.51 ± 0.13	175
H_2O, l	-285.830 ± 0.040	175
H_2O_2, l	-187.86	140
NaF, aq	-575.69 ± 0.65	175
NaOH:112H_2O, aq	-469.647	140
HF, g	-273.30 ± 0.70	175
HCl, g	-93.31 ± 0.10	175
HCl:1000H_2O, aq	-166.653 ± 0.004	107
HCl:2000H_2O, aq	-166.770 ± 0.004	107
HCl:2638H_2O, aq	-166.808 ± 0.004	107
HCl:2825H_2O, aq	-166.819 ± 0.004	107
HCl:6150H_2O, aq	-166.900 ± 0.004	107
Br_2, aq	-2.594 ± 0.042	107
HBr, g	-36.32 ± 0.16	175
HBr:2000H_2O, aq	-121.215 ± 0.004	107
HBr:3000H_2O, aq	-121.265 ± 0.004	107
HI, g	26.50 ± 0.10	175
HI:300H_2O, aq	-56.379 ± 0.0017	107
HCN, ao	107.1	140
PF_5, g	-1593.590 ± 0.895	107
P_4H_{10}, am	-3041.77	140
H_3PO_3, aq	-958.771 ± 1.787	107

H_3PO_4, c	−1285.981 ± 1.368	107
H_3PO_4:$40H_2O$, aq	−1295.443 ± 1.046	107
H_3PO_4:$4000H_2O$, aq	−1299.210 ± 1.046	107
H_3PO_4:$5000H_2O$, aq	−1299.424 ± 1.046	107
H_3PO_4:$10000H_2O$, aq	−1300.323 ± 1.046	107
$H_4P_2O_7$, c	−2248.458 ± 3.464	107
$SOCl_2$, l	−245.6 ± 4.2	108
SO_2Cl_2, l	−394.1 ± 4.2	108
CH_4, g	−74.5 ± 0.4	129
C_2H_6, g	−83.8 ± 0.4	129
C_4H_{10}, g	−125.6 ± 0.7	129
C_6H_6, l	49.0 ± 0.6	129
C_6H_{14}, l	−198.7 ± 0.8	129
MeOH, l	−239.1 ± 0.3	129
EtOH, l	−277.5 ± 0.4	129
PrOH, l	−302.6 ± 0.5	129
i-PrOH, l	−318.1 ± 0.5	129
BuOH, l	−327.3 ± 0.4	129
i-BuOH, l	−334.7 ± 0.9	129
PhOH, c	−165.1 ± 0.8	129
Et_3N, l	−127.7 ± 0.6	129
Et_3NHCl, c	−379.7 ± 1.0	129
Et_2NH, l	−103.7 ± 1.2	129
Et_2NH_2Cl, c	−358.6 ± 1.4	129
Me_2PhN, l	47.7 ± 3.2	129
$Me_2PhNHCl$, c	−151.0 ± 3.8	129

REFERENCES

1 J.P. Coleman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valey, 1987, and references cited therein.
2 C.A. McAuliffe, Comprehensive Coordination Chemistry, Vol. 2, Pergamon, London, 1987, pp. 989–1066.
3 T. Ziegler and A. Rauk, Inorg. Chem., 18 (1979) 1755.
4 S. Xiao, W.C. Trogler, D.E. Ellis and Z. Berkovich-Yellin, J. Am. Chem. Soc., 105 (1983) 7033.
5 D.S. Marynick, J. Am. Chem. Soc., 106 (1984) 4064.
6 M.R.A. Blomberg, U.B. Brandemark, P.E.M. Siegbahn, K.B. Mathisen and G. Karlstöm, J. Phys. Chem., 89 (1985) 2171.
7 (a) M. Braga, Inorg. Chem., 24 (1985) 2702.
(b) M. Braga, Quim. Nova, 11 (1988) 71.
8 J.G. Verkade, Coord. Chem. Rev., 9 (1972/73) 1.
9 (a) H.J. Plastas, J.M. Stewart and S.O. Grim, J. Am. Chem. Soc., 91 (1969) 4326.
(b) H.J. Plastas, J.M. Stewart and S.O. Grim, Inorg. Chem., 2 (1963) 723.
10 A.J. Carty, P.C. Chieh, N.J. Taylor and Y.S. Wong, J. Chem. Soc. Dalton Trans., (1976) 572.
11 P.B. Hitchcock and P. Pye, J. Chem. Soc. Dalton Trans., (1977) 1457.
12 L. Pauling, Acta Crystallogr. Sect. B, 34 (1978) 746.

13 R. Mason and D.W. Meek, Angew. Chem. Int. Ed. Engl., 17 (1978) 183.

14 C.G. Christoph, J. Halpern, G.P. Khare, Y.B. Koh and C. Romanowski, Inorg. Chem., 20 (1981) 3029.

15 F.A. Cotton, D.J. Darensbourg and W.H. Ilsley, Inorg. Chem., 20 (1981) 578.

16 (a) A.G. Orpen and N.G. Connelly, Organometallics, 9 (1990) 1206.
(b) B.J. Dunne, R.B. Morris and A.G. Orpen, J. Chem. Soc. Dalton Trans., (1991) 653.

17 H. Liu, K. Eriks, A. Prock and W.P. Giering, Organometallics, 9 (1990) 1758 and references cited therein.

18 W.D. Horrocks and R.C. Taylor, Inorg. Chem., 2 (1963) 723.

19 (a) R.J. Angelici, J. Inorg. Nucl. Chem., 28 (1966) 2627.
(b) R.J. Angelici and M.D. Malone, Inorg. Chem., 6 (1967) 1731.

20 W. Strohmeier and F.J. Muller, Chem. Ber., 100 (1967) 2812.

21 W.A. Graham, Inorg. Chem., 7 (1968) 315.

22 R.P. Stewart and P.M. Treichel, Inorg. Chem., 7 (1968) 1943.

23 C.H. Tolman, J. Am. Chem. Soc., 92 (1970) 2953.

24 C. Barbeau and J. Turcotte, Can. J. Chem., 54 (1976) 1603.

25 T. Bartik, T. Himmler, H.-G. Schulte and K. Seevogel, J. Organomet. Chem., 272 (1984) 29.

26 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J. Chem. Soc. Dalton Trans., (1973) 1028.

27 (a) G.M. Bodner, Inorg. Chem., 14 (1975) 1933.
(b) G.M. Bodner, Inorg. Chem., 14 (1975) 2694.
(c) G.M. Bodner, M.P. May and L.E. McKinney, Inorg. Chem., 19 (1980) 1951.

28 G.M. Gray and C.S. Kraihanzel, J. Organomet. Chem., 241 (1983) 201.

29 K.H. Whitmire and T.R. Lee, J. Organomet. Chem., 282 (1985) 95.

30 (a) L. Falvello and M. Gerloch, Inorg. Chem., 19 (1980) 472.
(b) M. Gerloch, L.R. Hanton and M.R. Manning, Inorg. Chim. Acta, 48 (1981) 205.

31 (a) J.R. Phillips and J.I. Zink, Inorg. Chem., 25 (1986) 1503.
(b) H. Chang and J.I. Zink, Inorg. Chem., 25 (1986) 2736.
(c) H. Jaw and J.I. Zink, Inorg. Chem., 27 (1988) 3421.

32 C. Diaz and N. Yutronic, Polyhedron, 6 (1987) 503.

33 (a) J.A. Tossell, J.H. Moore and J.C. Giordan, Inorg. Chem., 24 (1985) 1100.
(b) J.C. Giordan, J.H. Moore and J.A. Tossell, Acc. Chem. Res., 19 (1986) 281.

34 L.W. Yarbrough II and M.B. Hall, Inorg. Chem., 17 (1978) 2269.

35 B. Shaw, J. Chem. Soc. Chem. Commun., (1979) 104.

36 (a) J. Behan, R.A.W. Johnstone and R.J. Puddephatt, J. Chem. Soc. Chem. Commun., (1978) 444.
(b) G.M. Bancroft, T.C.S. Chan and R.J. Puddephatt, Inorg. Chem., 22 (1983) 2133.
(c) R.J. Puddephatt, G.M. Bancroft and T.C.S. Chan, Inorg. Chim. Acta, 73 (1983) 83.
(d) G.M. Bancroft, L. Dignard-Bailey and R.J. Puddephatt, Inorg. Chem., 25 (1986) 3675.

37 H. Daamen, A. Oskam and D.J. Stufkens, Inorg. Chim. Acta, 38 (1980) 71.

38 (a) B.E. Bursten, D.J. Darensbourg, G.E. Kellog and D.L. Lichtenberger, Inorg. Chem., 25 (1986) 3675.
(b) D.L. Lichtenberger and M.E. Jatcko, Inorg. Chem., 31 (1992) 451.

39 (a) B.V. Johnson, P.J. Ouseph, J.S. Hsieh, A.L. Steinmetz and J.E. Shade, Inorg. Chem., 18 (1979) 1797.
(b) B.V. Johnson, A.L. Steinmetz and P.J. Ouseph, J. Coord. Chem., 14 (1985) 103.

40 R.L. Cook and J.G. Morse, Inorg. Chem., 23 (1984) 2332.

41 (a) J.W. Hershberger and J.K. Kochi, Polyhedron, 9 (1983) 929.
(b) D.J.K. Kuchynka, C. Amatore and J.D. Kochi, Inorg. Chem., 25 (1986) 4087.

42 M. Gerloch and L.R. Hanton, Inorg. Chem., 20 (1981) 1046.

43 T. Allman and R.G. Goel, Can. J. Chem., 60 (1982) 716.

44 (a) M.N. Golovin, Md.M. Rahman, J.E. Belmonte and W.P. Giering, Organometallics, 4 (1985) 1981.
(b) Md.M. Rahman, H.-Y. Liu, A. Prock and W.P. Giering, Organometallics, 6 (1987) 650.
(c) Md.M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, Organometallics, 8 (1989) 1.
(d) H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, Organometallics, 9 (1990) 1758.

45 H.C. Clark and M. Hampden-Smith, Coord. Chem. Rev., 79 (1987) 229.

46 (a) C.A. Tolman, J. Am. Chem. Soc., 92 (1970) 2956.
(b) C.A. Tolman, Chem. Rev., 77 (1977) 313.

47 (a) T. Bartik, P. Heimbach and T. Himmler, J. Organomet. Chem., 276 (1984) 399.
(b) T. Bartik and T. Himmler, J. Organomet. Chem., 293 (1985) 343.

48 A. Immirzi and A. Musco, Inorg. Chim. Acta, 25 (1977) L41.

49 L. Stahl and R.D. Ernst, J. Am. Chem. Soc., 109 (1987) 5673.

50 W.C. Trogler and L.G. Marzilli, J. Am. Chem. Soc., 96 (1974) 7589.

51 W.C. Trogler and L.G. Marzilli, Inorg. Chem., 14 (1975) 2942.

52 J.T. DeSanto, J.A. Mosbo, B.N. Storhoff, P.L. Bock and R.E. Bloss, Inorg. Chem., 19 (1980) 3086.

53 P. Heimbach, J. Kluth, H. Schenkluhn and B. Weimann, Angew. Chem. Int. Ed. Engl., 19 (1980) 570.

54 D.J. Darensbourg and R.L. Kump, Inorg. Chem., 17 (1978) 2680.

55 M. Basato, J. Chem. Soc. Dalton Trans., (1986) 217.

56 A. Immirzi, A. Musco and B.E. Mann, Inorg. Chim. Acta, 21 (1977) L37.

57 (a) G. Ferguson, P.J. Roberts, E.C. Alyea and M. Khan, Inorg. Chem., 17 (1978) 2965.
(b) E.C. Alyea, G. Ferguson and A. Somogyvari, Inorg. Chem., 21 (1982) 1369.

58 J.D. Smith and J.D. Olivier, Inorg. Chem., 17 (1978) 2585.

59 (a) L. Xing-Fu, X. Ying-Ting, F. Xi-Zhang and S. Peng-Nian, Inorg. Chim. Acta, 116 (1986) 75.
(b) L. Xing-Fu, F. Xi-Zhang, X. Ying-Ting, W. Hai-Tung, S. Jie, L. Li and S. Peng-Nian, Inorg. Chim. Acta, 116 (1986) 85.
(c) L. Xing-Fu, S. Tian-Gi, S. Guang-Li and S. Peng-Nian, Inorg. Chim. Acta, 129 (1987) 227.
(d) L. Xing-Fu, S. Tian-Gi, S. Guang-Li and S. Peng-Nian, Inorg. Chim. Acta, 129 (1987) 235.
(e) L. Xing-Fu, S. Peng-Nian, G. Ao-Ling and L. Jing-Ci, Inorg. Chim. Acta, 129 (1987) 245.

60 J. Marçalo and A. Pires de Matos, Polyhedron, 8 (1989) 2431.

61 (a) C.A. Streuli, Anal. Chem., 32 (1960) 985.
(b) W.A. Henderson, Jr. and C.A. Streuli, J. Am. Chem. Soc., 82 (1960) 5791.

62 W.A. Henderson, Jr. and S.A. Buckler, J. Am. Chem. Soc., 82 (1960) 5794.

63 H. Goetz and A. Sidhu, Justus Liebigs Ann. Chem., 682 (1968) 71.

64 T.A. Mastryukova and M.I. Kabachnik, Russ. Chem. Rev., 38 (1969) 795.

65 (a) S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mallard, J. Phys. Chem. Ref. Data, 17 (1988) Suppl. 1.
(b) S.G. Lias, J.F. Liebman and R.D. Levin, J. Phys. Chem. Ref. Data, 13 (1984) 695.

66 R.V. Hodges, J.L. Beauchamp, A.J. Ashe III and W.-T. Chan, Organometallics, 4 (1985) 457.

67 F.A. Cotton, Inorg. Chem., 3 (1964) 702 and references cited therein.
68 S.R. Gunn and L.G. Green, J. Phys. Chem., 60 (1961) 779.
69 G.K. Johnson, J.G. Malm and W.N. Hubbard, J. Chem. Thermodyn., 4 (1972) 879.
70 (a) E. Neale and L.T.D. Williams, J. Chem. Soc., (1952) 4535.
   (b) E. Neale and L.T.D. Williams, J. Chem. Soc., (1954) 2156.
71 T. Charnley and H.A. Skinner, J. Chem. Soc., (1953) 450.
72 L.A. Niel'son and G.V. Seryakov, Russ. J. Inorg. Chem., 5 (1960) 548.
73 D.R. Stull, Ind. Eng. Chem., 39 (1947) 517.
74 R.R. Holmes, J. Phys. Chem., 64 (1960) 1295.
75 M. van Driel and H. Gerding, Rec. Trav. Chim., 60 (1941) 943.
76 (a) A. Finch, P.J. Gardner and I.H. Wood, J. Chem. Soc., (1965) 746.
   (b) A. Finch, P.J. Gardner and A. Hameed, J. Inorg. Nucl. Chem., 32 (1970) 2869.
77 (a) R.H. Davies, A. Finch, P.J. Gardner, A. Hameed and M. Stephens, J. Chem. Soc. Dalton Trans., (1976) 556.
   (b) P.J. Gardner, Thermochim. Acta, 205 (1992) 65.
78 L.H. Long and J.F. Sackman, Trans. Faraday Soc., 53 (1957) 1606.
79 E.J. Rosenbaum and C.R. Sandberg, J. Am. Chem. Soc., 62 (1940) 1622.
80 W. Lautsch, A. Tröber, W. Zimmer, L. Mehner, W. Linck, H.-M. Lehmann, H. Brandenberger, H. Korner, H.-J. Metschker, K. Wagner and R. Kaden, Z. Chem., 3 (1963) 415.
81 W.F. Lautsch, P. Erzberger and A. Tröber, Wiss. Z. Tech. Hochsch. Chem. Carl Schorlemmer Leuna-Merseburg, 1 (1958/59) 31.
82 W.F. Lautsch, Chem. Technol., 10 (1958) 419.
83 H.W. Thompson and J.W. Linnett, Trans. Faraday Soc., 32 (1936) 681.
84 K.G. Kruif, J.M. Herman and P.G. van der Berg, J. Chem. Eng. Data, 26 (1981) 359.
85 C.L.T. Chernick and H.A. Skinner, J. Chem. Soc., (1956) 1401.
86 A.V. Nikolaev, Y.A. Afanasev and A.D. Starostin, Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk, 14 (1968) 3.
87 D.R. Kirklin and E.S. Domalski, J. Chem. Thermodyn., 20 (1988) 743.
88 A.A. Grigor'ev, Y.V. Kontrat'ev and A.V. Suvorov, Zh. Obshch. (Engl. Transl.), 54 (1985) 1725.
89 (a) M.V. Forward, S.T. Bowden and W.J. Jones, J. Chem. Soc. Proc., Part V (1949) 3121.
   (b) M.V. Forward and S.T. Bowden, J. Chem. Soc., (1949) 121.
90 C.L.T. Chernick, H.A. Skinner and C.T. Mortimer, J. Chem. Soc., (1955) 3936.
91 E. Neale, L.T.D. Williams and V.T. Moores, J. Chem. Soc., (1956) 422.
92 D.P. Evans, W.C. Davies and W.J. Jones, J. Chem. Soc., (1930) 1310.
93 P.A. Fowell and C.T. Mortimer, J. Chem. Soc., (1959) 2913.
94 A. Finch, P.J. Gardner, K.S. Hussain and R.A. Melaugh, J. Chem. Thermodyn., 7 (1975) 881.
95 E. Neale and L.T.D. Williams, J. Chem. Soc., (1955) 2485.
96 J.R. Van Wazer and L. Maier, J. Am. Chem. Soc., 86 (1964) 811.
97 F. Ebel and E. Bretscher, Helv. Chim. Acta, 12 (1929) 450.
98 J.B. Ott and W.F. Giauque, J. Am. Chem. Soc., 82 (1960) 1308.
99 A.P. Claydon, P.M. Fowell and C.T. Mortimer, J. Chem. Soc., (1960) 3284.
100 A.D. Starostin, A.V. Nikolaev and Y.A. Afanas'ev, Izv. Akad. Nauk SSSR Ser. Khim. (Engl. Transl.), (1966) 1255.
101 A.V. Nikolaev, Y.A. Afanas'ev and A.V. Starostin, Dokl. Akad. Nauk. SSSR (Engl. Transl.), 168 (1966) 489.
102 J. Huinink, K. van Miltenburg, H.A.J. Oonk, A. Schuijff and P. Groen, J. Chem. Eng. Data, 34 (1989) 99.

103 A.F. Bedford and C.T. Mortimer, J. Chem. Soc., (1960) 1622.

104 G. Geisler, K. Quitzsch and M. Kockert, Z. Phys. Chem. (Leipzig), 218 (1961) 37.

105 A.F. Bedford, D.M. Heinekey, I.T. Millar and C.T. Mortimer, J. Chem. Soc., (1962) 2932.

106 G. Al Takhin, H.A. Skinner and A.A. Zaki, J. Chem. Soc. Dalton Trans., (1984) 371.

107 J.B. Pedley (Ed.), "CATCH" Computer Analysis of Thermochemical Data, University of Sussex, Brighton, 1972.

108 J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, 1977.

109 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.

110 G. Pilcher and H.A. Skinner, in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Wiley, New York, 1985, pp. 43–90.

111 G. Pilcher, in F.R. Hartley (Ed.), The Chemistry of Organophosphorus Compounds, Vol. 1, Wiley, New York, 1990, pp. 127–136.

112 V.I. Tel'noi and I.B. Rabinovich, Russ. Chem. Rev. (Engl. Transl.), 49 (1980) 603.

113 (a) A.R. Dias, J.A. Martinho Simões, C. Teixeira, C. Airoldi and A.P. Chagas, J. Organomet. Chem., 335 (1987) 71.
(b) A.R. Dias, J.A. Martinho Simões, C. Teixeira, C. Airoldi and A.P. Chagas, J. Organomet. Chem., 361 (1989) 319.
(c) A.R. Dias, J.A. Martinho Simões, C. Teixeira, C. Airoldi and A.P. Chagas, Polyhedron, 10 (1991) 1433.

114 A.J. Head and W.D. Good, in S. Sunner and M. Månsson (Eds.), Experimental Chemical Thermodynamics, Vol. 1, Pergamon Press, Oxford, 1979, Chap. 9.

115 M. Ducros and H. Sannier, Thermochim. Acta, 75 (1984) 329.

116 V.V. Ovchinnikov, Yu.G. Safina, R.A. Cherkasov and A.N. Pudovik, Zh. Obshch. Khim. (Eng. Transl.), 58 (1988) 1853.

117 J.A. Martinho Simões and J.L. Beauchamp, Chem. Rev., 90 (1990) 629.

118 S.P. Nolan, D.P. Stern and T.J. Marks, J. Am. Chem. Soc., 111 (1989) 7844.

119 D.F. McMillen and D.M. Golden, Annu. Rev. Phys. Chem., 33 (1982) 493.

120 M.J. Wovkulich and J.D. Atwood, J. Organomet. Chem., 184 (1979) 77.

121 K.E. Lewis, D.M. Golden and G.P. Smith, J. Am. Chem. Soc., 106 (1984) 3905.

122 G.K. Yang, K.S. Peters and V. Vaida, Chem. Phys. Lett., 125 (1986) 566.

123 S.P. Nolan and C.D. Hoff, J. Organomet. Chem., 290 (1985) 365.

124 S.P. Nolan, R. López de la Vega, S.L. Mukerjee and C.D. Hoff, Inorg. Chem., 25 (1986) 1160.

125 S.L. Mukerjee, S.P. Nolan, C.D. Hoff and R. López de la Vega, Inorg. Chem., 27 (1988) 81.

126 S.P. Nolan, R. López de la Vega, S.L. Mukerjee, A.A. Gonzalez, K. Zhang and C.D. Hoff, Polyhedron, 7 (1988) 1491.

127 A.A. Gonzalez, K. Zhang, S.P. Nolan, R. López de la Vega, S.L. Mukerjee and C.D. Hoff, Organometallics, 7 (1988) 2429.

128 K. Zhang, A.A. Gonzalez, S.L. Mukerjee, S.-J. Chou, C.D. Hoff, K.A. Kubat-Martin, D. Barnhart and G.J. Kubas, J. Am. Chem. Soc., 113 (1991) 9170.

129 J.B. Pedley, R.D. Naylor and S.P. Kirby, Thermochemical Data of Organic Compounds, Chapman and Hall, London, 2nd edn., 1986.

130 B. Venkataraman, H. Hou, Z. Zhang, S. Chen, G. Bandukwalla and M. Vernon, J. Chem. Phys., 92 (1990) 5338.

131 C.D. Hoff, J. Organomet. Chem., 282 (1985) 201.

132 R.J. Angelici and C.M. Ingemanson, Inorg. Chem., 8 (1969) 83.

133 P. Boudeville and A. Darchen, Inorg. Chem., 30 (1991) 1663.

134 H.E. Bryndza, P.J. Domaille, W. Tam, L.K. Fong, R.A. Paciello and J.E. Bercaw, Polyhedron, 7 (1988) 1441.
135 H.E. Bryndza, P.J. Domaille, R.A. Paciello and J.E. Bercaw, Organometallics, 8 (1989) 379.
136 A.M. Stolzenberg and M. Scozzafava, Organometallics, 6 (1987) 2214.
137 W. Partenheimer and E.F. Hoy, J. Am. Chem. Soc., 95 (1973) 2840.
138 W. Partenheimer and E.F. Hoy, Inorg. Chem., 12 (1973) 2805.
139 C.A. Tolman, D.W. Reutter and W.C. Seidel, J. Organomet. Chem., 117 (1976) C30.
140 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
141 C.A. Tolman, W.C. Seidel and L.W. Gosser, J. Am. Chem. Soc., 96 (1974) 53.
142 L.W. Gosser and C.A. Tolman, Inorg. Chem., 9 (1970) 2350.
143 R.J. McKinney and D.C. Roe, J. Am. Chem. Soc., 108 (1986) 5167.
144 C.A. Tolman, J. Am. Chem. Soc., 96 (1974) 2780.
145 C.A. Tolman, W.C. Seidel and L.W. Gosser, Organometallics, 2 (1983) 1391.
146 H. Schenkluhn, W. Scheidt, B. Weimann and M. Zähres, Angew. Chem. Int. Ed. Engl., 18 (1979) 401.
147 W. Partenheimer, Inorg. Chem., 11 (1972) 743.
148 A. Sen, J.-T. Chen, W.M. Vetter and R.R. Whittle, J. Am. Chem. Soc., 109 (1987) 148.
149 W. Partenheimer, J. Am. Chem. Soc., 98 (1976) 2779.
150 L.E. Manzer and C.A. Tolman, J. Am. Chem. Soc., 97 (1975) 1955.
151 W. Partenheimer and E.H. Johnson, Inorg. Chem., 12 (1973) 1274.
152 P.B. Dias, A.R. Dias, H.G. Alt and J.A. Martinho Simões, to be published.
153 A.R. Dias, P.B. Dias, H.P. Diogo, A.M. Galvão, M.E. Minas da Piedade and J.A. Martinho Simões, Organometallics, 6 (1987) 1427.
154 M.D.M.C. Ribeiro da Silva, Tese de Doutoramento, Universidade do Porto, 1985.
155 M.A.V. Ribeiro da Silva and M.D.M.C. Ribeiro da Silva, J. Organomet. Chem., 393 (1990) 359.
156 P.B. Dias, M.D.M.C. Ribeiro da Silva, M.A.V. Ribeiro da Silva and J.A. Martinho Simões, to be published.
157 M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald and A.N. Syverud, J. Phys. Chem. Ref. Data, 14 (1985) Suppl. 1.
158 V.P. Glushko and V.A. Medvedev, Thermal Constants of Materials, Akademii Nauk, Moscow, 1972.
159 C.T. Mortimer, Rev. Inorg. Chem., 6 (1984) 233.
160 G. Boxhoorn, J.M. Ernsting, D.J. Stufkens and A. Oskam, Thermochim. Acta, 42 (1980) 315.
161 G. Boxhoorn, A.C. Jesse, J.M. Ernsting and A. Oskam, Thermochim. Acta, 27 (1978) 261.
162 D.L.S. Brown, J.A. Connor and H.A. Skinner, J. Chem. Soc. Faraday Trans. 1, 70 (1974) 1649.
163 G. Al-Takhin, J.A. Connor, G. Pilcher and H.A. Skinner, J. Organomet. Chem., 265 (1984) 263.
164 M.K. Geno and J. Halpern, J. Am. Chem. Soc., 109 (1987) 1238.
165 (a) M. Tilset and V.D. Parker, J. Am. Chem. Soc., 111 (1989) 6711; 112 (1990) 2843.
(b) M. Tilset, in J.A. Martinho Simões (Ed.), Energetics of Organometallic Species, Kluwer, Dordrecht, 1992, pp. 109–129.
166 G. Kiss, K. Zhang, S.L. Mukerjee, C. Hoff and G.C. Roper, J. Am. Chem. Soc., 112 (1990) 5657.
167 J.R. Sowa, Jr., V. Zanotti, G. Facchin and R.J. Angelici, J. Am. Chem. Soc., 113 (1991) 9185.
168 J.R. Sowa, Jr., V. Zanotti, G. Facchin and R.J. Angelici, J. Am. Chem. Soc., 114 (1992) 160.

169 A. Poë, ACS Symp. Ser. 155, American Chemical Society, Washington, DC, 1981, p. 135.
170 J.U. Mondal and D.M. Blake, Coord. Chem. Rev., 47 (1982) 205.
171 G. Pacchioni and P.S. Bagus, Inorg. Chem., 31 (1992) 4391.
172 (a) K.J. Lee and T.L. Brown, Inorg. Chem., 31 (1992) 289.
    (b) T.L. Brown, Inorg. Chem., 31 (1992) 1286.
173 S.L. Mukerjee, R.F. Lang, T. Ju, G. Kiss, C.D. Hoff and S.P. Nolan, Inorg. Chem., 31 (1992) 4885.
174 L. Luo and S.P. Nolan, Organometallics, 11 (1992) 3483.
175 J.D. Cox, D.D. Wagman and V.A. Medvedev (Eds.), CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.