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Notes

Determination of the Basicity of 1,1′-Bis(diphenylphosphino)metallocenes

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Summary: The heat of protonation for 1,1′-bis(diphenylphosphino)ferrocene (dppf) and 1,1′-bis(diphenylphosphino)ruthenocene (dppr) was determined by titration calorimetry using CF_3SO_3H in 1,2-dichloroethane. The $-\Delta H_{HP}$ values are 18.8(2) kcal/mol for dppf and 19.5(3) kcal/mol for dppr. The basicity of these phosphines is lower than other bidentate phosphines. In comparison to a phenyl group, the cyclopentadienyl rings of a ferrocenyl group are more π-accepting, and therefore, the basicity of dppf and dppr is lower than that of PPh_3. In addition, the heat of protonation of dppr is not significantly different from that of dppf.

Introduction

Monodentate (PR_3) and bidentate phosphines ($R_2P\frown PR_2$) are some of the most commonly used ligands in organometallic and coordination chemistry. By varying the organic substituents of phosphine ligands, the electronic and steric properties of compounds containing the phosphines can be altered. This in turn can influence the reactivity of the compounds, particularly those that serve as catalysts. For example, palladium catalysts used in the Heck reaction are very sensitive to the steric and electronic nature of the phosphine ligands.[1] In hydroformylation reactions using chelate phosphine ligands, the selectivity can be influenced by the electronic nature of the R groups.[2] Additional studies have shown that polymerization catalysts using nickel require bulky ligands in order for the reaction to occur with high specificity.[3]

Numerous studies have been performed to understand the steric and electronic parameters of phosphines. For monodentate phosphines, steric effects are typically described by Tolman's cone angles, while chelate phosphines are described in terms of bite angle.[4] One method for investigating the electronic nature of phosphines and phosphine-containing complexes is titration calorimetry.[5] This technique has been used to measure the basicity of phosphines ($-\Delta H_{HP}$) (eq 1) or

$$R_3P + CF_3SO_3H \xrightarrow{DCE} [R_3PH^+CF_3SO_3^-];\quad \Delta H_{HP} \quad (1)$$

phosphine-containing complexes ($-\Delta H_{HM}$) (eq 2) by

$$L_nM + CF_3SO_3H \xrightarrow{DCE} [L_nMH^+CF_3SO_3^-];\quad \Delta H_{HM} \quad (2)$$

determining the heat of protonation using triflic acid in 1,2-dichloroethane (DCE). The $-\Delta H_{HP}$ values for several monodentate and bidentate phosphines have been reported; as more electron-donating substituents are added to phosphorus, the $-\Delta H_{HP}$ values become more positive.[5,6] For example, trialkylphosphines give $-\Delta H_{HP}$ values that are approximately 10 kcal/mol greater than triarylphosphines.[5] Variations are also seen using substituted aryl groups; for example, P(*p*-tolyl)$_3$ is more basic than $P(p\text{-}C_6H_4Cl)_3$.[5] This effect on basicity is primarily due to electronic factors rather than sterics.

The basicity of bidentate phosphines is complicated by the presence of the two phosphorus atoms. Both phosphorus atoms have the capability of being protonated by acid, and this implies that two enthalpy values can be obtained (eq 3). The $-\Delta H_{HP1}$ and $-\Delta H_{HP2}$ values

$$\begin{gathered} R_2P\frown PR_2 + H^+ \xrightarrow{DCE} HR_2P\frown PR_2{}^+CF_3SO_3{}^-;\quad \Delta H_{HP1} \\ HR_2P\frown PR_2{}^+ + H^+ \xrightarrow{DCE} HR_2P\frown PR_2{}^{2+}(CF_3SO_3{}^-)_2;\quad \Delta H_{HP2} \end{gathered} \quad (3)$$

for a number of bidentate phosphines have been determined.[6] These data show that altering the R groups affects the basicity of the phosphines as seen in dppm (R = Ph, $-\Delta H_{HP1} = 22.0$ kcal/mol) as compared to dmpm (R = Me, $-\Delta H_{HP1} = 31.0$ kcal/mol).[6] A second factor in the basicity of bidentate phosphines is the group bridging the two phosphorus atoms. In the series $Ph_2P(CH_2)_n$-PPh_2 (n = 1−6), as the chain length (n) increases, $-\Delta H_{HP2}$ becomes more positive. This is a result of the electron-withdrawing group ($-PHPh_2{}^+$) being further away from the site of the second protonation, thereby making the second phosphorus more basic.[6] In addition,

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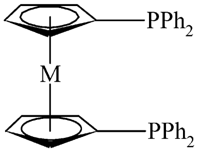

M = Fe; dppf
M = Ru; dppr

Figure 1. 1,1′-Bis(diphenylphosphino)metallocenes.

when $n \geq 4$, all of the $-\Delta H_{HP1}$ values are approximately 25.0 kcal/mol.[6] Apparently, the increase in alkyl chain length no longer has an effect on the basicity, indicating the electron-donating ability of the alkyl chain reaches a maximum effect at greater chain lengths.[6,7]

The connectivity between the phosphorus atoms can be varied in ways other than altering the length of the alkyl bridging groups. For example, the value of $-\Delta H_{HP1}$ for 1,4-bis(diphenylphosphino)benzene (dppbz) is 21.3 kcal/mol. This is slightly less basic than dppe ($-\Delta H_{HP1}$ = 22.8 kcal/mol).[6] This difference is due to the phenyl backbone being electron withdrawing in comparison to alkyl chains.[6]

In addition to studying the free bidentate phosphines, the basicities of compounds containing bidentate and monodentate phosphine ligands have been measured using titration calorimetry.[7,8] The protonation that occurs in these reactions is typically at the metal center and not at the phosphorus atom. A series of calorimetric studies investigated metal complexes that differed only by varying the metal center from a given group. Generally, an increase in mass of the metal should be accompanied by an increase in the basicity of the compound.[9] An example of this trend is observed in the series of compounds *cis*-$M(CO)_2dppm_2$ (M = Cr, Mo, or W) where the $-\Delta H_{HM}$ values (kcal/mol) increase down the group.[7,8] While the $-\Delta H_{HM}$ values are sensitive to the metal center, the protonation of ligands at atoms that are distant from the metal center is less sensitive to changing the metal. For example, in the series $M(CO)_5(\eta^1\text{-dppm})$ (M = Cr, Mo, or W), the $-\Delta H_{HP}$ values for the dangling phosphorus atom increase slightly going down the group.[10]

All of the heat of protonation studies to date have investigated bidentate phosphines with hydrocarbon backbones. Bidentate phosphines containing organometallic backbones, such as 1,1′-bis(diphenylphosphino)ferrocene (dppf) and 1,1′-bis(diphenylphosphino)ruthenocene (dppr) (Figure 1), have received considerable attention particularly as ligands in catalysis.[11] Attempts to rationalize the reactivity of compounds containing dppf and dppr have mainly focused on differences in the bite angle of these bidentate phosphines.[12] To understand more about these phosphine ligands, the electronics of dppf and dppr need to be fully explored. By determining the basicity of dppf and dppr using titration calorimetry, the donor ability of these bidentate phosphines can be better understood.

Experimental Section

General Procedures. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) was purchased from Strem. 1,1′-Bis(diphenylphosphino)ruthenocene (dppr) was prepared according to the literature method.[11c] Diphenylguanidine (DPG), purchased from GFS Chemicals, and tris(hydroxymethyl)aminomethane (THAM), purchased from Aldrich, were used as standards for calorimetry. Triflic acid (CF_3SO_3H), purchased from Ozark Fluorine Specialties, was distilled under argon prior to use. HPLC grade DCE from Aldrich was purified according to literature procedures[13] and distilled over P_4O_{10} under argon prior to use. Dichloromethane (DCM) was distilled over CaH_2 under argon. The NMR data were obtained in $CDCl_3$ and DCM on a JEOL Eclipse 400 FT-NMR. The internal standard for ^1H NMR was TMS (δ = 0.00 ppm), while 85% H_3PO_4 was used as an external reference for the $^{31}P\{^1H\}$ NMR.

Protonation Reactions. The phosphines were protonated for characterization of the $dppfH_2^{2+}$ and $dpprH_2^{2+}$ products by dissolving 12.0 mg of phosphine in 1.00 mL of $CDCl_3$ in an NMR tube. To this solution, 2 equiv of CF_3SO_3H were added through the rubber septum using a syringe. The color of the solutions remained unchanged during the process. Yields of the protonated products were determined to be quantitative by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

$[dppfH_2]^{2+}[CF_3SO_3]_2^-$. ^1H NMR ($CDCl_3$): δ 7.78 (m, 14H), 7.66 (m, 8H), 4.90 (s, 4H), 4.85 (s, 4H). ^{31}P NMR ($CDCl_3$): δ 2.78 (s).

$[dpprH_2]^{2+}[CF_3SO_3]_2^-$. ^1H NMR ($CDCl_3$): δ 7.80 (m, 14H), 7.65 (m, 8H), 5.21 (s, 4H), 5.05 (s, 4H). ^{31}P NMR ($CDCl_3$): δ 2.80 (s).

Calorimetric Studies. The dppf and dppr heat of protonation values were measured on a Tronac Model 458 isoperibol calorimeter. The titrations were performed under argon, and each trial consisted of three phases, an initial heating phase calibration, titration, and a final heating phase calibration. Each portion was preceded by a baseline acquisition phase. Prior to use, all equipment was oven-dried and cooled in desiccators containing P_4O_{10}. The acid solution was prepared according to the literature procedure.[5] Each titration involved the addition of approximately 1.2 mL of a standardized 0.1 M triflic acid solution at a constant rate over 4 min to a ~1.3 mM solution of phosphine in 50 mL of DCE at 25.0 °C.[5] Data were collected in the Lab Works program and analyzed using Microsoft Excel. Four trials of each phosphine were performed, and the heat of protonation was calculated from the average of these trials. The values were corrected for the heat of dilution of the acid in DCE (−0.2 kcal/mol).[14] Two different standardized acid solutions were used for titration of the compounds. The average deviation from the mean is reported as the error.

Results and Discussion

The addition of 2 equiv of triflic acid resulted in the clean protonation of dppf and dppr. The protonation of dppf with HBF_4 has previously been described, and the ^{31}P NMR data in this report are in good agreement with the reported value.[15] In that study, the authors report the synthesis of $dppfH^+$ from equal molar amounts of dppf and $dppfH_2^{2+}$.[15] The electrochemistry of $dppfH^+$

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Table 1. NMR Investigation of dppf Protonation in DCM

temperature (°C)	acid equivalents	observed peaks (ppm)			
−30	1	6.57	3.38	−4.77	−20.0
	1.5	6.25	3.34	−4.81	
	2	3.35			
25	1	no distinct peaks observed			
	2	3.35			
50	1	−6.14			

Table 2. ΔH_{HP} Values for 1,1′-Bis(diphenylphosphino)metallocenes, Select Organophosphines, and Select Phosphine Complexes

phosphine	$-\Delta H_{HP}$, kcal/mol	metal complex	$-\Delta H_{HM}$, kcal/mol
dppr	19.5(3)	$Cr(CO)_2(dppm)_2$	25.5(1)[c]
dppf	18.8(2)	$Mo(CO)_2(dppm)_2$	29.7(3)[c]
PPh_3	21.2(1)[a]	$W(CO)_2(dppm)_2$	31.5(2)[c]

phosphine	$-\Delta H_{HP1}$; $-\Delta H_{HP2}$, kcal/mol	dangling phosphine	$-\Delta H_{HM}$, kcal/mol
dppm	22.0(1); 14.9(2)[b]	$Cr(CO)_5(\eta^1\text{-dppm})$	17.1(1)[d]
dpppent	24.8(2); 24.5(1)[b]	$Mo(CO)_5(\eta^1\text{-dppm})$	18.6(1)[d]
dppbz	21.3(1); 10.7(3)[b]	$W(CO)_5(\eta^1\text{-dppm})$	19.1(3)[d]

[a] Reference 5. [b] Reference 6. [c] Reference 8. [d] Reference 10.

was investigated and was very similar to that of $dppfH_2^{2+}$ due to the "moderately fast equilibrium" shown in eq 4.[15] This implies that there should not be

$$2\ dppfH^+ \rightleftharpoons dppf + dppfH_2^{2+} \qquad (4)$$

a significant difference between the $-\Delta H_{HP1}$ and $-\Delta H_{HP2}$ values for dppf.

To better understand the details of the protonation of dppf and dppr, a variable-temperature NMR study was preformed in DCM (Table 1). One equivalent of triflic acid was added to a solution of dppf, and the $^{31}P\{^1H\}$ NMR spectrum was recorded at −30 °C. The spectrum consisted of two broad peaks (6.57 and −20.0 ppm) and two sharp singlets (3.38 and −4.77 ppm). The broad peak at −20.0 ppm corresponds to unprotonated dppf. Upon warming to room temperature, the signals became indistinguishable from the baseline. Upon heating the sample to 50 °C, the NMR signal coalesced into one broad peak. An additional 0.5 equiv of triflic acid was added to the sample, and the $^{31}P\{^1H\}$ NMR spectrum was recorded at −30 °C. There was no peak observed for unprotonated dppf. In addition, the peaks at 6.25 and −4.81 ppm were less intense than the peak at 3.38 ppm, suggesting that the former correspond to the monoprotonated species. After an additional 0.5 equiv of acid had been added, the $^{31}P\{^1H\}$ NMR spectrum contained one peak at δ 3.35, corresponding to $dppfH_2^{2+}$. This indicates that there is fast exchange between dppf, $dppfH^+$, and $dppfH_2^{2+}$, implying that there is not a significant difference in the $-\Delta H_{HP1}$ and $-\Delta H_{HP2}$ values for dppf.

The heat of protonation for the reaction of dppf and dppr with triflic was measured using titration calorimetry (Table 2). Two equivalents of acid were added during the titration, but no change in the slope of the titration was noted (Figure 2), indicating that there are not significant differences in the $-\Delta H_{HP1}$ and $-\Delta H_{HP2}$ values for dppf or dppr. This differs from dppm, where the $-\Delta H_{HP1}$ is 7.1 kcal/mol greater than the $-\Delta H_{HP2}$, but is similar to 1,5-bis(diphenylphosphino)pentane (dppent), where $-\Delta H_{HP1}$ is only 0.3 kcal/mol greater than ΔH_{HP2}.[6]

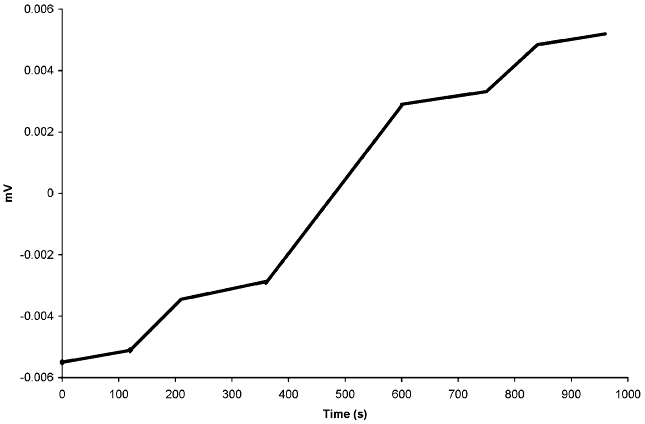

Figure 2. Titration of dppf.

The ferrocene backbone appears to isolate the $-PPh_2$ groups from each other, similar to long-chain alkyl groups. This can also been seen in the $^{31}P\{^1H\}$ NMR of $M(CO)_5(\eta^1\text{-}P^\frown P)$ where M = Cr, Mo, or W and $P^\frown P$ = dppf or dppm. In the dppm-containing compounds, the ^{31}P signal for the dangling phosphine is shifted upfield by 2.3 ppm on average.[10] However, the dangling phosphorus in the dppf compounds has a chemical shift at approximately −17.14 ppm,[16] nearly identical to the shift of uncoordinated dppf.[11a]

The heat of protonation values for dppf and dppr are lower than the $-\Delta H_{HP1}$ values observed for other bidentate phosphines.[6] Most of the bidentate phosphines investigated have an alkyl backbone, suggesting that the metallocene backbone of dppf and dppr is less donating than an alkyl group. The heat of protonation of bidentate phosphine with an aryl backbone, 1,1′-bis(diphenylphosphino)benzene (dppbz), has been measured;[6] dppbz is more basic than dppf and dppr, which indicates that the metallocene backbones are less donating than an aryl ring.

Numerous studies have investigated the electronic nature of ferrocenyl substituents. Although a ferrocenyl group (Fc) is considered to be more σ-donating than a methyl group on *para*-substituted benzenes,[17] Fc can also play the role of a π-acceptor. Most studies have shown Fc groups to be π-donating; however there is a recent report of the π-accepting nature of ferrocene. In $Cr(CNFc)_6$, the electronic properties of the complex are more akin to a chromium complex with aryl isocyanide ligands than alkyl-substituted isocyanides.[18] This is due to donation of the C≡N π-electrons into the π-orbitals of the Cp rings.[18] Prior to these findings, it was assumed that the electronic properties of isocyanoferrocene were similar to methyl isocyanide, but in reality the Fc fragment is closer to the electronics of aryl subsitituents. This means that the Fc backbone of dppf can act as a π-acceptor, making dppf similar to bidentate phosphines with aryl bridges rather than bidentate phosphines with alky bridges.

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Since dppf and dppr behave more like dppbz, in which the phosphorus atoms are bound to three aryl groups, the heat of protonation values of dppf and dppr can be compared to PPh_3.[5] Although the heat of protonation values for dppf and dppr are close to PPh_3, the values for the bidentate phopshines are a bit lower. The donor ability of the phosphorus atoms changes significantly upon the replacement of one phenyl with an Fc fragment, the difference between PPh_3 and dppf/dppr. In addition to protonation studies, this difference in donor ability can be seen in the average ν_{CO} values for related compounds containing PPh_3 and $FcPPh_2$. For example, the average ν_{CO} for $(PPh_3)(Re)(CO)_4Cl$ is 2013 cm^{-1}, while that for $(FcPPh_2)(Re)(CO)_4Cl$ is 2016 cm^{-1}.[19] The shift to higher wavenumbers upon replacement of a phenyl group with an Fc indicates that PPh_3 is a better donor than $FcPPh_2$. Therefore, it is not surprising that the $-\Delta H_{HP}$ values for dppf and dppr are slightly lower than for PPh_3.

A comparison of the effect of the metal in the metallocene on the basicity of the phosphine can also be made. The basicity of the metal increases going down a group, as seen in *cis*-$M(CO)_2(dppm)_2$ (M = Cr, M, or W).[7,8] This trend can also be seen in $Cp^*{}_2M$ (M = Ru or Os), compounds with structures and electronics similar to dppf and dppr. The $-\Delta H_{HM}$ values for the Ru and Os complexes are 19.0 and 26.2 kcal/mol, respectively, indicating that going down the group there is an increase in the basicity of the metal.[7,8] In addition, qualitative studies have indicated that Cp_2Ru is more basic than Cp_2Fe.[9,20] However, the metal has a significantly smaller effect on the basicity when protonation occurs at a site other than the metal center, such as in $M(CO)_5(\eta^1\text{-dppm})$ (M = Cr, Mo, or W).[10] In that series protonation occurs at the dangling phosphorus and there is only a 2.0 kcal/mol difference in the basicity of the Cr and W compounds.[10] As protonation of dppf and dppr occurs at the phosphorus atoms and not the metal centers, it is not surprising that dppr is not significantly more basic than dppf.

A number of catalytic studies have been performed comparing the activity of dppr versus dppf. The activity is highly dependent on the system. For example, $[PdCl_2(dppr)]$ is a more efficient catalyst than $[PdCl_2(dppf)]$ for the coupling of 2-bromobiphenyl and MgPhBr.[11c] However, in the catalytic amination of *p*-bromobutylbenzene, the opposite trend in catalytic activity is observed.[11b] In both cases, the activity is attributed to the bite angle of dppr as compared to dppf. In the hydrodebromination of 4,4′-dibromobiphenyl, the catalytic activity of $[PdCl_2(dppf)]$ was found to be superior to that of $[PdCl_2(PPh_3)_2]$.[21] The authors suggest a number of explanations including the "better σ-donor ability of dppf".[21] The results of this calorimetric study indicate that dppr and dppf are not better donors than PPh_3. In addition, the similar heat of protonation values of dppf and dppr suggest that the difference in catalytic activity is likely due to the bite angle rather than a difference in donor ability.

Conclusions

Titration calorimetry was used to measure the basicity of dppf and dppr in order to better understand the donor ability of these bidentate phosphines. The $-\Delta H_{HP}$ values for dppf and dppr are 18.8 and 19.5 kcal/mol, respectively. Unlike dppbz and other small alkyl chelates, both the ΔH_{HP1} and ΔH_{HP2} values for dppf and dppr are equivalent, suggesting that the metallocene backbone of the phosphine isolates the $-PPh_2$ groups. The heat of protonation values indicate that dppf and dppr are weaker donors than other bidentate phosphines with alkyl and aryl bridges. This is likely due to the π-accepting nature of the metallocene backbone. As seen in other systems where protonation occurs away from the metal center, the basicity increases slightly going down a group; dppr is not significantly more basic than dppf.

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