Formation and Reactions of Bis(phosphino)succinic Anhydrides

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A route to 2,3-bis(phosphino)succinic anhydrides and related compounds is described. The compounds are formed by reaction of a secondary phosphine with maleic anhydrides which bear a leaving group at the alkenic carbon atom. The reaction of bromomaleic anhydride with diphenylphosphine proceeds *via* diphenylphosphinomaleic anhydride. An acid-catalysed Michael addition leads to *cis*-2,3-bis(diphenylphosphino)succinic anhydride, which in turn rearranges to the *trans* isomer by an acid-catalysed process. The *trans* isomer was isolated as a hydrobromide. The formation of diphosphines from the corresponding maleic acids and esters has also been observed. A primary phosphine does not lead to a phosphinosuccinic anhydride.

Addition of a base to the bis(phosphino)succinic anhydride generally leads to the elimination of the phosphine moiety. However, the anhydride ring can be opened with sodium methoxide and a diphosphine, with both a carboxylic acid and a carboxylate ester moiety, is formed in moderate yield. Two conformers or isomers of this compound are obtained, both of which decarboxylate readily to give methyl 2,3-bis(diphenylphosphino)propanoate.

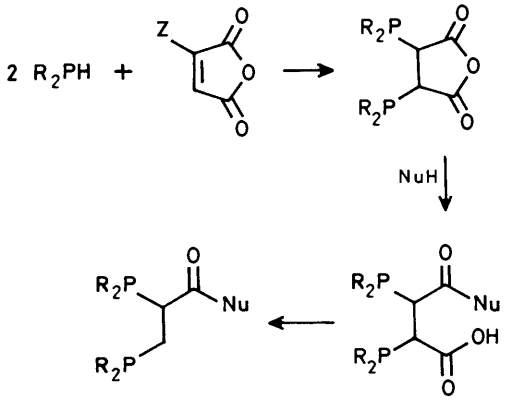
Co-ordination of the diphosphine system to Pt^{II} prevents both the elimination of secondary phosphine and the decarboxylation of carboxylic groups.

Various diphosphinoethanes with hydrocarbon substituents in the ethano bridge between the two phosphorus atoms have been prepared in the past. These investigations have led to several interesting chiral bis-phosphine ligands.[1] In these ligands the substituents are necessary to create a chiral centre in the bridge but apart from steric factors they do not exert an influence on the co-ordination behaviour of the diphosphine with transition metals. In our view, functional groups in the bridge could be of great interest since the functionality can be used to control the electronic nature of the phosphorus atom or can participate in the bonding of the metal. Previously, we have reported the preparation of functionalised mono-phosphines by a Michael addition of secondary phosphines to maleic anhydride.[2] In this paper we describe the formation of novel bis-phosphines *via* a sequence of addition and elimination steps in the reaction of secondary phosphines with bromomaleic anhydride and related compounds. We expected the anhydride moiety to react with nucleophiles (NuH) in a similar fashion to the reactions of diphenylphosphinosuccinic anhydride,[2] to give a diphosphinosuccinic acid or a derivative thereof. Decarboxylation of such a compound may in turn lead to a monofunctionalised diphosphinoethane. These reactions would allow the synthesis of a series of novel diphosphinoethanes with various functional groups in the bridge.

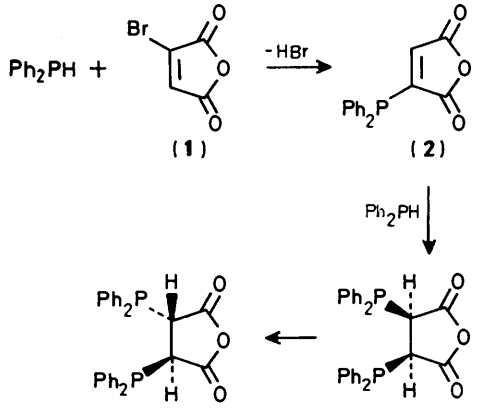
Related diphosphine systems have already been obtained by reaction of diphenylphosphine with acetylenedicarboxylic ester[3] (the product was isolated as a phosphonium salt), by a metal-mediated addition of the diphenylphosphine moiety to acetylenedicarboxylic ester,[4] and by reduction of a co-ordinated diphosphinomaleic imide.[5] Bis-2,3-(diphenylphosphinoyl)succinic esters have been prepared by a sequence of Michael reactions.[6]

Results

Bromomaleic anhydride (**1**) and two equivalents of diphenylphosphine react smoothly to give, eventually, *trans*-bis(diphenylphosphino)succinic anhydride (**4**). By monitoring the reaction between diphenylphosphine and (**1**) using NMR two consecutive intermediates (**2**) and (**3**) can be observed, which are rapidly converted into (**4**). A solution with a relatively high concentration of (**2**) and (**3**) can be obtained when the reaction



Z = Br, Cl *etc.*

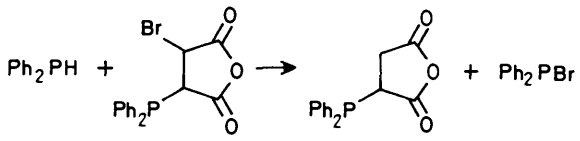


is carried out below 0 °C. However, it appears that under these conditions the life-time of these intermediates is still too short to permit their ^{13}C spectrum to be recorded. Fortunately, we discovered that more stable solutions of (**2**) and (**3**) are obtained when the acid HBr, which is an inevitable reaction product, is removed immediately upon its formation by the addition of solid $NaHCO_3$ to the reaction mixture. By using both $NaHCO_3$ and an excess of (**1**) we obtained a stable solution that was relatively rich in (**2**). All the NMR spectra of (**2**) are readily obtained by subtraction of the signals due to other compounds [*i.e.* (**1**), (**3**), (**4**), and diphenylphosphine]. The structure of (**2**) was unambiguously assigned on the basis of the spectra [^1H, ^{31}P, ^{13}C, $^{13}C\{^1H\}$ and ^{13}C (*J* modulated)] as diphenylphosphinomaleic anhydride (the data are presented in the Experimental section). By adding solid $NaHCO_3$ to the reaction mixture we also managed to obtain a solution of both the intermediate (**3**) and the eventual product (**4**), where the conversion of (**3**) into (**4**) is strongly retarded. From the NMR spectra [^1H, ^{31}P, ^{13}C, $^{13}C\{^1H\}$ and ^{13}C (*J* modulated)] we conclude that (**3**) and (**4**) are both symmetrical diphosphines because each contains two equivalent carbonyl groups and two equivalent (HCP) fragments. Thus (**3**) and (**4**) are geometrical, *i.e. cis* and *trans*, isomers.

cis- and *trans*-diphosphines show different features with respect to the ^{31}P chemical shift and the $^3J(PP)$ coupling constant. *trans*-Diphosphines have a ^{31}P chemical shift which is close to the value calculated from additivity constants, whereas the signals from *cis*-diphosphines are shifted to high field. The $^3J(PP)$ coupling constant in *cis*-diphosphines is very large compared with that of the corresponding *trans* isomer (100–150 and 15–40 Hz, respectively).[7–9] By simulation of the aliphatic signals in the ^1H NMR spectrum of (**4**) we obtained a value of 8 Hz for the $^3J(PP)$ coupling constant. The value of this constant for (**3**) could not be obtained from the proton spectrum as the hydrogens give rise to a virtual triplet, so it is obvious that the value must be considerably larger than 8 Hz. The coupling patterns of the CP carbons in the ^{13}C spectrum also clearly show that the $^3J(PP)$ coupling constant for (**3**) is much larger than that of (**4**). Thus the values of the chemical shifts and coupling constants for (**3**) and (**4**) are completely compatible with a *cis* and a *trans* structure, respectively (all of the data are given in the Experimental section). The structure of compound (**4**) was further established on the basis of the elemental analysis of both a mono- and a bis-hydrobromide (see the Experimental section) and its conversion into 1,2- bis(diphenylphosphino)ethane in *ca.* 30–40% yield by ring opening of the anhydride with water and subsequent decarboxylation.[2,10]

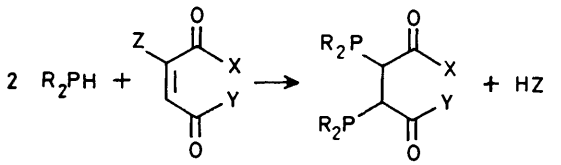
The reaction between diphenylphosphine and bromomaleic anhydride was investigated in various solvents. Most common organic solvents can be used provided that they do not react with the phosphine or the anhydride (see Table 1). In [$^2H_8$]toluene the product separates from the reaction mixture as a thick oil. Crystals of the mono-hydrobromide are obtained when diethyl ether is used, whereas the bis-hydrobromide crystallises from a reaction in dichloromethane (96% yield calculated on bromo compound, 48% calculated on the phosphorus compound). The mother liquor of the latter reaction still contains large amounts of the unprotonated diphosphine, and the addition of gaseous HBr to this solution leads to another crop of the bis-hydrobromide. With [$^2H_8$]tetrahydrofuran as the solvent the product remains in solution. The protons due to HBr give rise to a broadened peak at 10.6 ppm but coupling with the phosphorus atom is not observed. We have found that the diphosphines are not stable in THF solution. In a process that is slow with respect to the addition reaction, the phosphine moiety is cleaved from the organic skeleton and bromo(diphenyl)phosphine is formed. We have not examined the fate of the anhydride moiety.

An anomalous reaction occurs in $CDCl_3$. Diphenylphosphinosuccinic anhydride and diphenylbromophosphine are simultaneously formed with the expected product bis(diphenylphosphino)succinic anhydride. We believe that the by-products are either the result of a decomposition reaction as given above or of a reduction of the intermediary bromo(diphenylphosphino)succinic anhydride, which itself is not observed, by diphenylphosphine. In an independent experiment we showed that bromosuccinic anhydride is reduced by diphenylphosphine to succinic anhydride; however, instead of the expected bromo(diphenyl)phosphine, tetraphenyldiphosphine was obtained.



An interesting effect was observed in the conversion of the intermediary *cis*-diphosphine (**3**) into the *trans* isomer (**4**). It appears that an increase in the donicity constant *DN*[11] of the solvent leads to a decrease of the rate of this reaction. In toluene (*DN* = 0.1) the *cis* isomer was never observed; if it had been formed then the rate of the conversion must have been high. In THF (*DN* = 20) or in DMF (*DN* = 26.6) this conversion can be monitored by NMR spectroscopy. The $t_{1/2}$ values for the conversion are *ca.* 10 and 15 min, respectively. In the latter solvents the acid will be partially bonded to the solvent, *i.e.* the salts are dissociated, and these results suggest that the isomerisation is catalysed by protons.

We have briefly studied the addition reaction of the phosphine R_2PH, the conversion of the intermediates, and the stability of the final products as a function of R, X, Y, and Z



and the solvent. We used various secondary phosphines R_2PH and found that the reaction is tolerant to large variations in both the electronic and the steric nature of R_2PH. The results are compiled in Tables 1 and 2. We have observed that an increase of the χ value[12] of R_2PH, while the cone angle[12] is kept constant, leads to a decrease of the rate of the reaction (see Table 1, entries 2, 11, and 12). The result obtained with bis-(2-cyanoethyl)phosphine suggests that a decrease in the cone angle leads to an increase of the reaction rate. To summarise, small and electron-rich secondary phosphines react very fast, whereas large and electron-poor phosphines react relatively slowly. We also observed an effect exerted by the electronic nature of the groups R on the rate of the conversion of the intermediary *cis* isomer into the corresponding *trans* isomer. When the phosphorus atom bears electron-donating groups such as cyclohexyl or 2-methoxyphenyl, the *cis* compound is never observed; (if it is formed then it must be rapidly converted into the *trans* isomer). With other substituents such as Ph, 4-$CF_3C_6H_4$ and CH_2CH_2CN the *cis* compound is always observed. The conversion into the *trans* isomer is very slow when more strongly electron-withdrawing groups are present (see Table 1).

We have attempted to prepare diphosphine compounds by the double addition of primary phosphines RPH_2. However, we have found that primary phosphines react in a different

Table 1. Reaction[a] of R_2PH and bromomaleic anhydride at 20 °C.

Entry	R	Solvent	Conversion[b] (%)	t/min	NMR data[i] *cis*[j]	NMR data[i] *trans*[k]
1	Ph	[$^2H_8$]Toluene	30[c]	5	*m*	4.1 7.2
2	Ph	[$^2H_8$]THF	75[d]	15	4.4(12) −13.3	3.9 11.8
3	Ph	[$^2H_7$]DMF	25[e]	15		
4	Ph	CD_2Cl_2	90[d]	30		
5	Ph	[$^2H_6$]DMSO	*f*			
6	Ph	[$^2H_6$]Acetone	*g*			
7	*c*-C_6H_{11}	[$^2H_8$]Toluene	100	*l*	*m*	3.7 22
8	*c*-C_6H_{11}	[$^2H_8$]THF	100[h]	5	*m*	3.2 24.2
9	2-$CH_3OC_6H_4$	[$^2H_8$]THF	100	5	*m*	3.9 −2.8
10	3-$CH_3C_6H_4$	[$^2H_8$]Toluene	100	5	*m*	4.2 7.5
11	4-$CH_3C_6H_4$	[$^2H_8$]THF	85	15	*m*	3.9 10.8
12	4-$CF_3C_6H_4$	[$^2H_8$]THF	45	1 400	4.9(12) −13.9	*l*
13	CH_2CH_2CN	[$^2H_8$]THF	70	30	4.0(12) −18.0	3.7 −4.9

[a] Both reactants 0.1–0.2 mol dm^{-3}. [b] Conversion of R_2PH to adducts monitored by ^{31}P NMR spectroscopy. [c] In 1 h at 20 °C a small amount of Ph_2PBr is formed δ_P 71.7. [d] Ph_2PBr is formed over 24 h. [e] In addition, 50% conversion into unidentified product δ_P −13.5. [f] Reaction of Ph_2PH with the solvent δ_P 28. [g] Addition of Ph_2PH to the solvent δ_P 11. [h] After formation of the product decomposition to (*c*-$C_6H_{11})_2PBr$ is observed. [i] In the order ^1H, ^{31}P. [j] ^1H virtual triplet, N in parentheses. [k] ^1H typical AA'XX' spectrum. [l] Extremely slow conversion into the *trans* compound. [m] Not observed.

Table 2. Conversion of Ph_2PH as a function of X, Y, and Z.[a]

Entry	X, Y	Z	Solvent	Conversion (%)	t/h	T/°C
1	X + Y = O	Br	[$^2H_8$]THF	75	0.25	20
2	X + Y = O	Cl	[$^2H_8$]THF	100	0.5	20
3	X + Y = O	OAc	[$^2H_8$]Toluene	30	5.5	20
4	X = Y = OH	Br	[$^2H_8$]THF	90	75	20[b]
5	X = Y = OH	Br	[$^2H_5$]Pyridine	0	0.3	20
6	X = Y = OH	Br	[$^2H_5$]Pyridine	*c*		70
7	X = Y = OCH_3[d]	Br	[$^2H_5$]THF	50	28	60
8	X = Y = OC_2H_5	OTs	[$^2H_5$]THF	0	65	70
9	X = Y = OC_2H_5	OTs	[$^2H_5$]Toluene	80	65	100

[a] XC(O)CHCZC(O)Y. [b] At 70 °C, decarboxylation of the product. [c] Non-selective reaction, eight products. [d] 70% of the *cis* isomer.

way with bromomaleic anhydride. Instead of adducts, they give an appreciable yield of a triphosphine. This compound is the result of a redox reaction and was tentatively identified as 1,3-dibromo-1,2,3-triphenyltriphosphine.[13]

It appears that cyclic maleic derivatives are the more reactive compounds. Maleic esters and acids require long reaction times or elevated reaction temperatures.

From a mechanistic point of view, the reaction of bromomaleic acid is interesting. In this case the very first addition product of the secondary phosphine to the acid, 2-bromo-3-diphenylphosphinosuccinic acid, is observed by NMR spectroscopy as a transient intermediate [δ_P 2.6; δ_H 4.00 (dd, *J* 1.5, 12 Hz) and 4.65 (dd, *J* 3.5, 12 Hz)]. We found an unexpectedly large difference between the reactivity of the maleic ester with Z = OTs and that of the corresponding ester with Z = Br. The toluene-*p*-sulphonate does not react in conditions where the reaction of the bromo compound with diphenylphosphine is fast.

In order to prepare a family of functionalised diphosphinoethanes by transformation of bis(phosphino)succinic anhydride we planned a sequence of reactions. Firstly, careful removal of the acid HZ with amines or other weak bases such as K_2CO_3 should lead to the acid-free diphosphine. Secondly, opening of the anhydride ring with nucleophiles (water, alcohols, or secondary amines) would lead to a diphosphinosuccinic acid derivative. Subsequent decarboxylation or transformation of the resulting carboxylic groups leads to other functionalised diphosphinoethanes.

Indeed HBr is readily removed from (**4**)·HBr by a number of weak bases such as triethylamine, dibenzylamine, aqueous K_2CO_3 *etc.*, but, unfortunately, it appears that (**4**) decomposes in the presence of bases. The most abundant reaction products are diphenylphosphine, diphenylphosphine oxide and the mono-oxide of tetraphenyldiphosphine. If the deprotonation of (**4**)·HBr is carried out in acetone, then 2-diphenylphosphinopropan-2-ol, the adduct between diphenylphosphine and acetone, is obtained in high yield. Addition of solid K_2CO_3 or $NaHCO_3$ at the beginning of the reaction does not lead to a pure product. The nature of the decomposition products clearly shows that under slightly basic or neutral conditions, elimination of the phosphine moiety occurs. This reaction prevents the isolation of the unprotonated bis(diphenylphosphino)succinic anhydride (**4**). Therefore, we attempted to remove the acid and to open the anhydride ring in one reaction step. However, in most of the cases, elimination of the phosphine moiety is still the predominant reaction and opening of the anhydride proved to be slow. For instance, no amide is formed in the reaction of (**4**)·HBr with dibenzylamine at 60 °C. Good results were obtained with both (**4**)·HBr and *trans*-bis[di-(2-cyanoethyl)phosphino]succinic anhydride hydrobromide using sodium methoxide as both the nucleophile and the base. The expected half-ester of the corresponding diphosphinosuccinic acid with the correct analytical data (see the Experimental section) is obtained, albeit in moderate yield. The products exist of two conformers of the expected *threo* compound or, alternatively, of a mixture of the *threo* and the

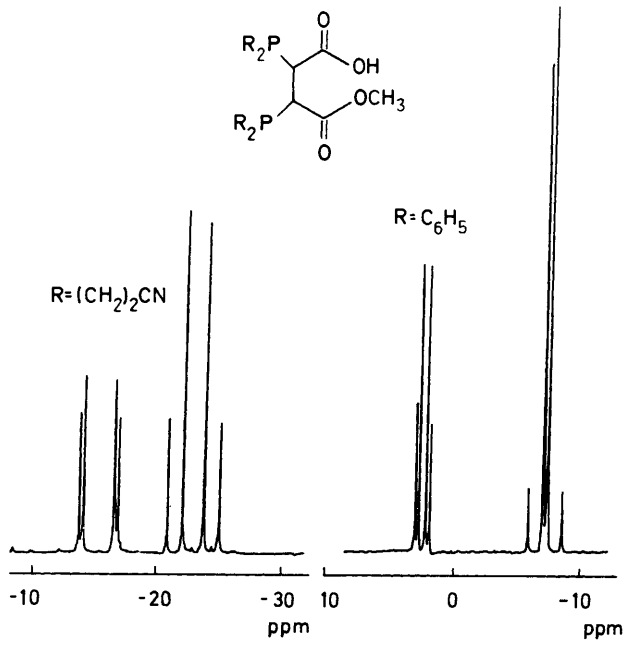


Figure. ^{31}P NMR spectra (101 MHz; ^{1}H decoupled) of methyl hydrogen bis(phosphino)succinate. Each spectrum consists of two sets of AB signals.

erythro isomers (see the Figure). The NMR spectra do not clearly discriminate between the two possibilities.

The mixture obtained from the reaction of (**4**)·HBr decarboxylates smoothly when refluxed in chloroform. Methyl 2,3-bis(diphenylphosphino)propanoate is obtained as the only product. Saponification of this compound to the corresponding acid with acid or base was unsuccessful because of extensive elimination of a diphenylphosphine moiety.

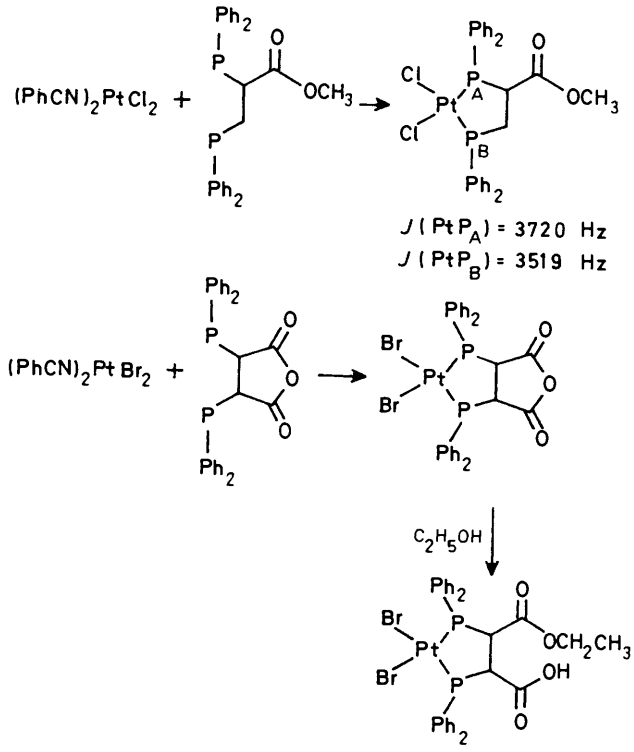
We obtained 2,3-bis(diphenylphosphino)succinic acid in an impure state by reaction of diphenylphosphine with bromomaleic acid at 70 °C. At this temperature one of the carboxy groups is rapidly lost by decarboxylation and the corresponding bis(diphenylphosphino)propanoic acid is formed. The second carboxy group undergoes decarboxylation very slowly at this temperature.

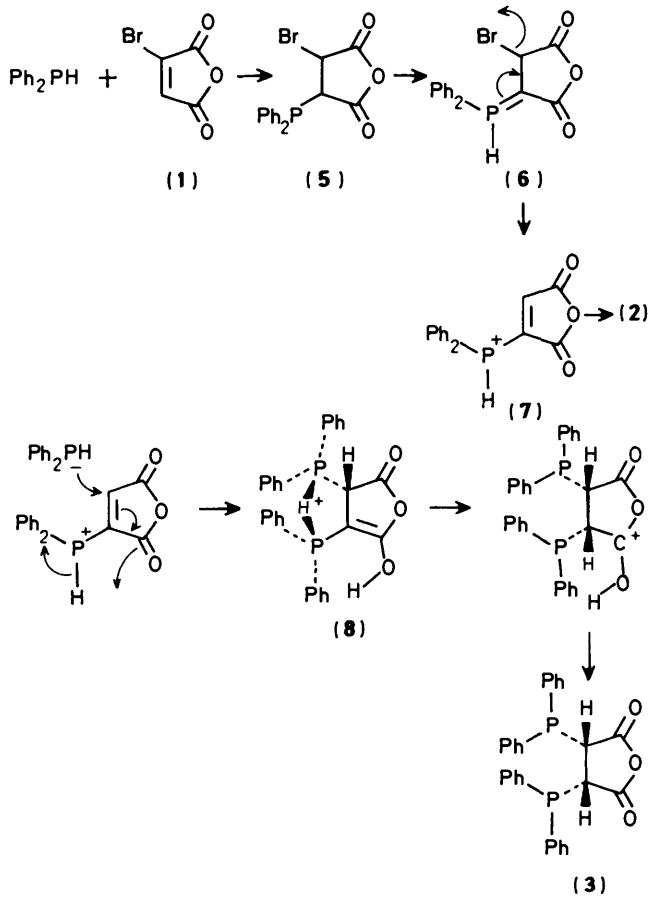
Reaction of methyl 2,3-bis(diphenylphosphino)propanoate with bis(benzonitrile)platinum dichloride leads to the expected diphosphine complex. The values of the ^{1}J(PtP) coupling constants convincingly demonstrate the steering of the χ parameter of the phosphine by the carboxylate moiety: $J(PtP_A) = 3\,720$ Hz, whereas $J(PtP_B) = 3\,519$ Hz. We encountered serious difficulties in the preparation of pure and acid-free bis(phosphino)succinic anhydrides. Therefore, we attempted to prepare metal complexes of (**4**) using the crude reaction mixture, and, indeed, the expected platinum complex was readily obtained. Moreover, transformation of the anhydride moiety now proved to be possible without the deleterious elimination of the phosphine moiety as observed in the unco-ordinated molecule. Reaction of the complex with ethanol leads to a platinum complex with a co-ordinated diphosphinosuccinic mono-ester. This complex is thermally very stable; refluxing in *o*-dichlorobenzene overnight does not result in the elimination of phosphine from the succinic moiety or in decarboxylation of the carboxylic acid group.

Discussion

We have observed that both the electronic and the steric nature of the secondary phosphine have an effect on the rate of the addition reaction. An increase in the χ value of the secondary phosphine, with the steric properties remaining constant, leads to a decrease of the rate, as does an increase in the cone angle at constant χ value. These phenomena are consistent with a Michael addition of the secondary phosphine to the activated alkene.

Diphenylphosphinomaleic anhydride is formed from bromomaleic anhydride (**1**) and the secondary phosphine as depicted in the reaction scheme below. Attack of the secondary phosphine at the unsubstituted alkene carbon atom in a Michael-type addition leads to a phosphinobromosuccinic anhydride (**5**). At no point did we observe this compound itself, but a related adduct was formed as a transient intermediate in the reaction of diphenylphosphine with bromomaleic acid. Rapid elimination of HBr may occur from an isomeric compound, the ylide (**6**). This would mean that the phosphine moiety acts as a built-in base which abstracts the hydrogen ion; with another array of hydrocarbon substituents such ylides are stable compounds.[14] Alternatively, the secondary phosphine attacks the substituted alkene carbon atom and the phosphinomaleic anhydride is formed by an addition–elimination mechanism. The addition of a diphenylphosphine molecule to diphenylphosphinomaleic anhydride (**2**) clearly is acid-catalysed, because in the presence of solid $NaHCO_3$ the addition is strongly retarded. This is readily understood since (**7**) is a better Michael acceptor than the unprotonated molecule. It is also feasible that this proton plays a role in the subsequent reactions: when the secondary phosphine attacks the unsubstituted carbon of diphenylphosphinomaleic anhydride (protonated form) the oxygen atom of the carbonyl group adjacent to the protonated phosphine moiety becomes negatively charged and it is likely that the proton is transferred from the originally protonated phosphorus atom to this oxygen atom. The result is a protonated enol tautomer of diphenylsuccinic anhydride. Loss of a proton and tautomerisation leads to either (**3**) or (**4**). It appears that despite considerable steric crowding the *cis* isomer (**3**) is formed as a kinetic product. (A similar preference for the formation of a





thermodynamically unfavourable *cis* isomer was observed in the addition of radicals to substituted maleic anhydrides).[15] This may be accounted for in two ways. Structure (**8**) with a bridging hydrogen atom is likely to be formed. Acid-catalysed enolisation, while the bridging structure remains intact, must lead to the *cis* compound since two interconnected five-membered rings are present. Alternatively, the bridging proton in (**8**) is transferred to the unsaturated carbon atom either directly or *via* a base to give (**3**). The isomerisation of the *cis* isomer to the *trans* isomer is also acid-catalysed. In the presence of solid $NaHCO_3$ or in solvents that are able to bind the acid HZ (high *DN* value) this rearrangement is retarded. Furthermore, there is a relationship between the rate of the *cis–trans* isomerisation and the electronic nature of the phosphorus atoms. The reaction is relatively slow when the phosphorus atoms bear electron-withdrawing groups (high χ value). This suggests that the rearrangement takes place when a phosphorus atom is protonated. The reaction apparently proceeds *via* the breaking of a CH bond and subsequent transfer of the proton to the other side of the molecule.

Both a carbonyl group and a phosphine moiety are able to stabilise a carbanionic centre. Therefore, the hydrogens in the α-position of (**4**) will be relatively strongly acidic and so readily abstracted by a base. This abstraction can occur intermolecularly or intramolecularly by the built-in base, *i.e.* the phosphine moiety. From the resulting carbanion, a phosphine moiety can be readily eliminated, unless the medium is acidic. Thus, due to the relatively strong acidity of the α-hydrogens in diphosphines bearing either a succinic anhydride moiety or a carboxylate moiety the compounds are inherently unstable. This impedes the isolation of acid-free products and strongly limits transformations of the organic skeleton by standard organic chemistry. The elimination reaction does not occur when the diphosphine is bonded to a platinum atom. This suggests that the lone electron-pairs of the phosphorus atoms may be involved in the elimination reaction, *i.e.* that the abstraction of the hydrogen occurs intramolecularly by the phosphine moiety.

Compounds with a phosphinoacetic acid fragment decarboxylate at relatively low temperatures, and the mechanism of this reaction has been reported.[10] The lone electron-pair of the phosphorus atom plays a crucial role in this mechanism. When no lone pair is present as in the phosphine sulphide or in the protonated molecule the decarboxylation is very slow or does not occur. Our finding that decarboxylation does not occur when a mono-ester of bis(diphenylphosphino)succinic acid is co-ordinated to platinum is well in line with this mechanism.

Conclusions

Bis(phosphino)succinic anhydrides and related compounds are readily accessible from relatively simple starting materials. The compounds are formed by a sequence of interesting reactions including an acid-catalysed Michael addition and a remarkable acid-catalysed *cis–trans* rearrangement. In solution the products appear to possess limited stability, however, they can be isolated in high yield as the hydrobromide salt. Both in acidic and basic media the phosphine moiety is cleaved from the organic skeleton by decomposition reactions. This strongly diminishes the preparative use of the bis(phosphino)succinic anhydrides. We have obtained a mono-ester of bis(diphenylphosphino)succinic acid by reaction of the anhydride with sodium methoxide. Decarboxylation of this compound gives a bis(phosphino)propanoate in high yield. However, the ready elimination of a phosphine moiety from these molecules also frustrates further useful synthetic chemistry. By contrast, co-ordination of the bis(phosphino)succinic anhydride to platinum allows transformations of the anhydride moiety.

Experimental

All operations with air-sensitive materials were performed in an argon atmosphere. [$^2H_8$]THF was made free of peroxides with basic alumina and dried with sodium wire. Diethyl ether and THF were distilled in an argon atmosphere from sodium diphenylketyl. Starting materials which are not mentioned were obtained commercially or were prepared by well established synthetic methods. Bis(4-methylphenyl)phosphine was prepared from the corresponding tertiary phosphine by cleavage with sodium in liquid ammonia. Bis(2-methoxyphenyl)phosphine [b.p. 133 °C/0.03 mmHg, $\delta_P(CDCl_3)$ −73.2 ppm] was prepared by reduction of the corresponding oxide with AlH_3.[16] Bis(3-methylphenyl)phosphine [b.p. *ca.* 130 °C/12 mmHg, $\delta_P(CDCl_3)$ −40.7 ppm] and bis(4-trifluoromethylphenyl)phosphine [b.p. 142 °C/12 mmHg, $\delta_P(CDCl_3)$ −41.8 ppm] were prepared by thermal disproportionation of the corresponding secondary phosphine oxides. *N*-Benzylbromomaleimide,[17] dimethyl bromomaleate,[18] diethyl tosylmaleate,[19] and bromosuccinic anhydride[20] were prepared according to literature procedures. NMR spectra were obtained with Bruker 90, 250, and 400 MHz instruments. The data are given below; carbon–phosphorus couplings are given in parentheses and carbon–hydrogen couplings are given in square brackets. Coupling constants are given in Hz and chemical shifts in ppm.

Typical NMR Experiment.—A solution was prepared from bromomaleic anhydride (17.7 mg, 0.10 mmol) [$^2H_8$]THF (0.5 cm^3). The phosphine (0.20 mmol) was added *via* a syringe. The

mixture was homogenised and the reaction was monitored by NMR spectroscopy. The reaction products are colourless but generally purple or red solutions were obtained.

NMR Data of Diphenylphosphinomaleic Anhydride (**2**).—To a solution of bromomaleic anhydride (0.70 mmol) in [$^2H_8$]THF (3.5 cm^3), in a 25 cm^3 Schlenk flask were added $NaHCO_3$ (500 mg) and diphenylphosphine (0.28 mmol) at −78 °C. The mixture was stirred vigorously overnight at room temperature, to give a mixture which was relatively rich in compound (**2**). δ_P −16.7 ppm; δ_H 6.64 [1 H, d, ^3J(PH) 2.5; δ_C 155.3 {(−29) [3], CP}, 137.6 {(4) [184], CH}, 165.4 {(20), CO}, 163.6 {(5), CO}, 132.6 {(−6), *i*}, 134.7 {(21), [160], *o*}, 129.7 {(3) [160], *m*}, and 130.8 {[160], *p*}.

NMR Data of cis-2,3-*Bis(diphenylphosphino)succinic Anhydride* (**3**).—To a solution of bromomaleic anhydride (0.37 mmol) in [$^2H_8$]THF (2.5 cm^3), contained in a 10 mm NMR tube were added $NaHCO_3$ (450 mg) and diphenylphosphine (0.74 mmol). The mixture was shaken mechanically for 4 h, centrifuged, and subsequently cooled in an ice bath. The ^{31}P NMR spectrum showed that the *cis*:*trans*:Ph_2PH ratio was 4:3:3. After subtraction of the signals due to Ph_2PH and the *trans* isomer, the most important signals could be identified and assigned without ambiguity. δ_P −12.3 ppm; δ_H 4.4 {2 H, virtual triplet, N = 12}; δ_C 44.5 {second-order pattern N = 12, [138], CP}, and 169.7 {virtual triplet N = 8, CO}.

trans-2,3-*Bis(diphenylphosphino)succinic Anhydride Bis(hydrobromide)* (**4**)·2HBr.—To a solution of bromomaleic anhydride (7.0 g, 40 mmol) in dichloromethane (100 cm^3) was added diphenylphosphine (14.7 g, 79 mmol) at 0 °C. The mixture was stirred for 4 h at room temperature, and white crystals separated from the solution. The product was collected by filtration, washed with dichloromethane (2 × 25 cm^3) and dried *in vacuo* (0.1 mmHg). Yield: 12.0 g, (19 mmol; 48%) of the *title compound*. The yield can be improved to 80% when the combined washings and the mother liquid are concentrated to *ca.* 50 cm^3 and gaseous dry HBr is bubbled through the solution until saturation (Found: C, 53.35; H, 3.95; Br, 25.6; P, 9.74. $C_{28}H_{24}Br_2O_3P_2$ requires C, 53.36; H, 3.84; Br, 25.36; P, 9.84%).

NMR δ_P([$^2H_8$]THF) 10.0 ppm; δ_H([$^2H_8$]THF) 3.9 (2 H, AA′XX′ pattern, ^3J(HH) = 4.6 ^3J(PP) = 8, ^1J(PH) = 1.8 ^3J(PH) = 14.7; δ_C([$^2H_8$]THF) 45.6 {^1J(PC) = −34, ^2J(PC) = 18) [142], CP}, 170.0 {[6], CO}, 134.6 {(−17), *i*}, 134.9 {(−15), *i*}, 134.6 {(20), *o*}, 135.3 {(21), *o*}, 130.1 {(6), *m*}, 130.2 {(7), *m*}, 131.0 {*p*}. The chemical shifts depend slightly on the concentration of the compound.

trans-2,3-*Bis(diphenylphosphino)succinic Anhydride Hydrobromide* (**4**)·HBr.—To a solution of bromomaleic anhydride (7.5 g, 42 mmol) in diethyl ether (100 cm^3) was added diphenylphosphine (15.8 g, 84 mmol) at 0 °C. The mixture was stirred for an hour at room temperature. The yellow precipitate was filtered off and washed with diethyl ether (3 × 20 cm^3). After being dried *in vacuo*, the *title compound* (16.3 g, 30 mmol, 71%) was obtained (Found: C, 61.35; H, 4.3; Br, 14.4; P, 11.4. $C_{28}H_{23}BrO_3P_2$ requires C, 61.22; H, 4.22; Br, 14.55; P, 11.28%).

Reduction of Bromosuccinic Anhydride with Diphenylphosphine.—To a solution of bromosuccinic anhydride (0.1 mmol) in [$^2H_8$]THF (0.5 cm^3) was added diphenylphosphine (0.16 mmol) *via* a syringe. After 2 h at room temperature the NMR spectra were recorded. Succinic anhydride (identified by ^1H NMR spectroscopy) and tetraphenyldiphosphine (identified by ^{31}P NMR spectroscopy) were found to be the products.

Methyl Hydrogen 2,3-*Bis(diphenylphosphino)succinate.*—To a solution of bromomaleic anhydride (17.7 g, 0.1 mol) in THF (150 cm^3) was added diphenylphosphine (37.2 g, 0.2 mol) at 0 °C. The solution turned red and was stirred for 3 h at room temperature. Subsequently, the mixture was added over 3 min to a solution of sodium (5.8 g, 0.25 mol) in methanol (200 cm^3), maintained at −78 °C. The cooling bath was removed and the mixture was stirred until room temperature was reached. Most of the solvents were removed *in vacuo* and the remaining yellow solid residue was suspended in water. Hydrochloric acid was added to adjust the solution to pH 2. The organic material was extracted with dichloromethane, and the organic layer was washed with water and dried on $MgSO_4$. Filtration followed by evaporation of the solvent left a yellow oil, which crystallised on trituration with diethyl ether. A white solid (20.6 g, 42 mmol, 42%) was obtained (Found: C, 69.4; H, 5.4; P, 12.55. $C_{29}H_{26}O_4P_2$ requires C, 69.60; H, 5.24; P, 12.38%). The NMR spectrum (in $CDCl_3$) showed two sets of signals δ_P −6.8 and −7.4 ppm, [^3J(PP) = 120]; δ_H 3.80 (1 H) and 3.62 (1 H); and δ_P 2.3 and 3.3, [^3J(PP) = 32.6]; δ_H *ca.* 3.75, [^3J(PH) = *ca.* 8] (see the Figure).

Methyl 2,3-*Bis(diphenylphosphino)propanoate.*—A solution of 2,3-bis(diphenylphosphino)succinic acid, monomethyl ester (10.0 g, 21 mmol) in chloroform (100 cm^3) was refluxed for 16 h at a bath temperature of *ca.* 70 °C. Evaporation of the solvent by distillation left a brown gum (9.0 g), crystallisation of which from methanol afforded white crystals (6.2 g, 14 mmol, 68%). NMR tube experiments revealed that the decarboxylation reaction gave a quantitative yield of the title compound. The brown gum obtained in the preparation, however, contained some diphenylphosphine oxide and other decomposition products. It is likely that decomposition can be avoided by more careful removal of the solvent. (Found: C, 73.7; H, 5.75; P, 13.55. $C_{28}H_{26}O_2P_2$ requires C, 73.50; H, 5.79; P, 13.39%). δ_P($CDCl_3$) 1.4 (P^1CH) and −17.9 (P^2CHH) ppm, ^3J(PP) = 24; δ_H($CDCl_3$) 3.17 (1 H, H^1CO), 2.14 (1 H, CH^2), and 2.59 (1 H, CH^3) respectively, $J(H^1H^2)$ = 2.8, $J(H^1H^3)$ = 12.3, $J(H^2H^3)$ = 13.5, $J(H^1P^1)$ = 2.8, $J(H^2P^1)$ = 9.1, $J(H^3P^1)$ = 5.7, $J(H^1P^2)$ = 9.2, and $J(H^2P^2)$ = 2.7, $J(H^3P^2)$ = 3.8; δ_C($CDCl_3$) 172.6 {(5.3), CO}, 51.5 {[151.5], OCH_3}, 42.3 {(23, 18) [129.0], CH^1P^1}, 28.9 {(19, 17) [127.5], $CH^2H^3P_2$}, 137.8 {(−13), *i*}, 137.3 {(−14), *i*}, 135.5 {(−18), *i*}, 134.8 {(−17), *i*}.

Complexation of trans-2,3-*Bis(diphenylphosphino)succinic Anhydride with* Pt^{II}.—A mixture of (**4**)·HBr and bis(benzonitrile)platinum dibromide in THF was left overnight at room temperature and subsequently refluxed for 1 h. The off-white crystals were removed by filtration, washed with diethyl ether and dried *in vacuo*. The yield of the expected diphosphine complex was 72%. The complex was almost insoluble in dichloromethane and acetone but dissolved well in DMF (Found: C, 40.9; H, 2.8; Br, 19.6; P, 7.8. $C_{28}H_{22}Br_2O_3P_2Pt$ requires C, 40.85; H, 2.69; Br, 19.4; P, 7.52%). NMR δ_P([$^2H_7$]DMF) 38.77 ppm [platinum satellites, ^1J(PPt) = 3 527]; δ_H([$^2H_7$]DMF) 4.18 (2 H).

Opening of the Anhydride Ring of (**4**)·$PtBr_2$.—A mixture of (**4**)·$PtBr_2$ (1.0 g) and ethanol (50 cm^3) was refluxed overnight, and a greyish material (1.0 g) was obtained by filtration.

NMR analysis (^1H and ^{31}P; [$^2H_7$]DMF) clearly showed that the mono-ester had been formed: δ_P 38.63 [^1J(PPt) 3 510] and 38.58 [^1J(PPt) 3 545], ^2J(PP) = 7; δ_H, 4.2 (2 H, m, CHP), 3.88 and 3.99 (each 1 H, ABM_3 pattern, J(AB) = 11, J(AM) = 7, OCH_2). The greyish colour of the product and the elemental analysis indicated that some elemental platinum

had been formed in the reaction. Owing to the poor solubility of the complex, the metal could not be removed.

Methyl 2,3-Bis(diphenylphosphino)propanoate–Pt^{II} *Complex*.—A mixture of bis(benzonitrile)platinum dichloride (1.9 g, 4.0 mmol) and the ligand (1.9 g, 4.2 mmol) in benzene (100 cm^3) was refluxed for 25 min. A white solid precipitated, which was collected by filtration, washed with diethyl ether and dried *in vacuo* to give the expected diphosphine complex (2.2 g, 76%) (Found: C, 46.7; H, 3.65; Cl, 9.7; P, 8.65; rest 31.4. $C_{28}H_{26}Cl_2O_2P_2Pt$ requires C, 46.55; H, 3.63; Cl, 9.81; P, 8.57; rest 31.43%). $\delta_P(CDCl_3)$ 51.7 [^1J(PPt) = 3 720, PCH] and 30.0 [^1J(PPt) = 3 519, PCH_2]; ^2J(PP) = 7.3.

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