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A General Strategy for Increasing the Air Stability of Phosphines Including Primary Phosphines

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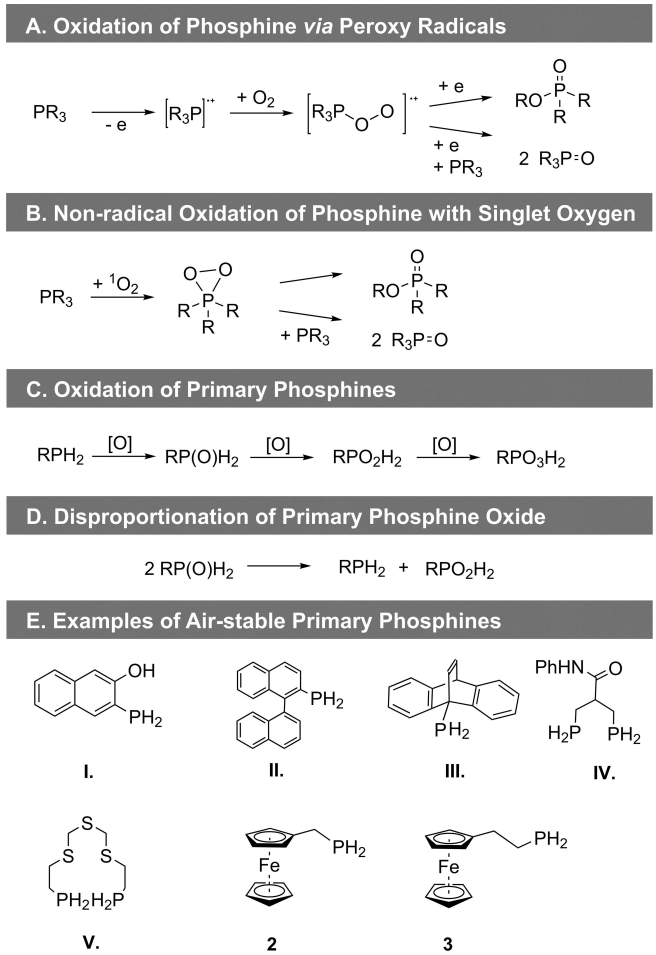
In memory of Edgar Niecke, a pioneer of modern phosphorus chemistry

A general approach for increasing the air-stability of various primary phosphines in the absence of kinetic stabilization is presented that contrasts with previous interpretations, which were limited to specific phosphines. This contribution shows the synthesis of a series of air-stable primary phosphines $Fc(CH_2)_nPH_2$, where $n = 0,1,2,3$; and Fc = ferrocenyl, and their corresponding isolable primary phosphine oxides. It was demonstrated that the ferrocene moiety exerts an antioxidant effect on the primary phosphine group, which is intermolecular, solvent dependent and increases with the electron density on the ferrocene moiety. Furthermore, we demonstrated that the presence of ferrocene in solution also inhibits the oxidation of other secondary and tertiary phosphines in air. Together our findings suggest that quenching of singlet oxygen is the actual reason for the antioxidant effect; this was experimentally confirmed by using other established singlet oxygen quenchers, thus demonstrating a key role of singlet oxygen in the aerobic oxidation of phosphines.

Introduction

Phosphines are of great relevance for important technological processes in catalysis, chemical synthesis and materials but also on a geo- and astrochemical level the occurrence and transformation of simple phosphines is in the focus of interest.[1] Extensive research has been carried out on the process of oxidation for trivalent phosphorus compounds.[2] When exposed to a radical initiator, it has been proven that phosphines undergo oxidation through peroxy radicals, ultimately resulting in the formation of phosphine oxide (as shown in Scheme 1A).[3] However, there is currently no unanimous agreement on the initial step in the mechanism of phosphine oxidation by atmospheric oxygen. In contrast, a reaction of sterically hindered phosphines with generated singlet oxygen has been shown to occur through a rare non-radical mechanism with formation of phosphadioxirane as the first reaction step (Scheme 1B).[4] Primary phosphines without a bulky substituent are especially air-sensitive and get oxidized in air spontaneously, often in a pyrophoric manner. The oxidation products are mixtures of the corresponding phosphine oxide, phosphinic and phosphonic acids (Scheme 1C).[5] In the literature, it is not common to specify



Scheme 1. Selected reactivity of organophosphorus compounds.

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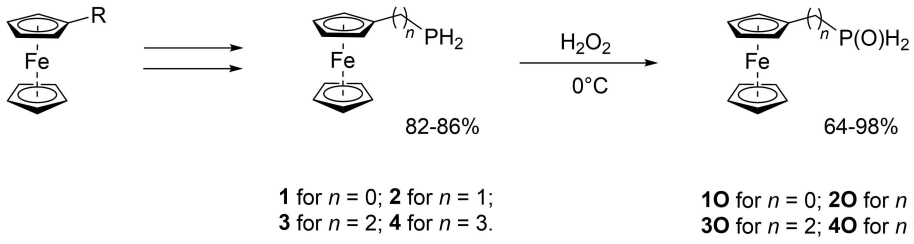
Part of a Special Collection on the p-block elements.



Scheme 2. Synthesis of ferrocene-based primary phosphines and primary phosphine oxides. Precursor for **1**: R = P_2S_4Fc; for **2**: R = $CH_2PO(OEt)_2$; for **3**: R = $(CH_2)_2Br$; for **4**: R = $(CH_2)_3Br$.

the exact composition of the oxidized mixture, as the situation is further complicated by the thermodynamic lability of $RP(O)H_2$, which spontaneously disproportionate into the respective primary phosphine and phosphinic acid (Scheme 1D).[6] That makes isolation of primary phosphine oxides particularly difficult with the exception of kinetically stabilized compounds.[7]

Despite what was mentioned before, there is an exciting group of air-stable primary phosphines where steric hindrance cannot be the protecting factor (Scheme 1E).[5a,b,8] Their stability is challenging to be rationalized. Typically, the backbone of these primary phosphines contains a heteroatom, conjugated system, or both. Therefore, their stability was assigned to the unique electronic nature of the phosphine group in these compounds. In a comprehensive study based on DFT calculations Higham *et al.* proposed a relationship between the stability of primary phosphines and the energy of the singly occupied molecular orbital (SOMO) of their radical cation.[9]

A recent report that oxidation of the known air-stable primary phosphine **2** gave also an isolable primary phosphine oxide,[10] led us to a deeper investigation of these compounds.

Results and Discussion

To start with, ferrocenyl phosphine **1** was synthesized following a literature procedure (Scheme 2).[11] Although it is not air-stable when compared to other primary phosphines, it only oxidizes very slowly. In our hands, less than 5% of **1** was oxidized in chloroform solution when stirred in the presence of air overnight (14 h). Surprisingly, controlled oxidation of **1** by hydrogen peroxide yielded phosphine oxide **1O** in 64% yield. The oxide was crystallized by sublimation (Figure 1) and did not further oxidize or disproportionate when stored as a solid for weeks.

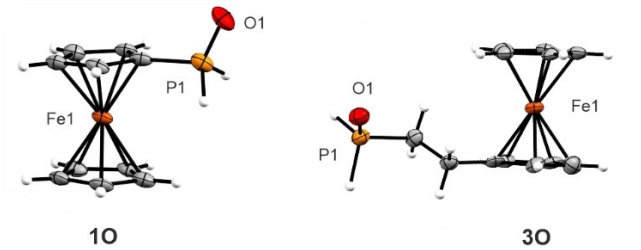


Figure 1. Molecular structures of phosphine oxides **1O** and **3O** derived from SC-XRD; for details see the Supporting Information.

The remarkable stability of methylene-bridged phosphine **2**[8f] and isolable **2O**[10a] led us to prepare their ethylene-bridged analogs. For this purpose, air-stable phosphine **3** was synthesized by an alternative procedure.[8g] As expected, its oxidation gave also isolable oxide **3O**.

In light of these findings, we realized that despite the rarity of phosphines **2** and **3**, a counterpart with a longer propylene spacer had not been prepared. Therefore, in a similar procedure, we synthesized bench stable phosphine **4** and oxide **4O** with 86% and 98% yields, respectively. The thermal stability of oxides **1O**-**4O** towards disproportionation under inert atmosphere (Scheme 1D) was studied with ^{31}P NMR spectroscopy with the temperature intervals in Table 1 showing the beginning and full disproportionation, respectively. The most labile is oxide **1O** whereas the most resistant oxide **4O** fully disproportionated at 100 °C.

Comparing the structures of **1** without a spacer and **4** with the phosphorus-ferrocene distance of four chemical bonds indicated that it is unlikely to attribute the antioxidant effect of the ferrocene fragment on the phosphine group to inductive or mesomeric effects along the bond path. That led us to a deeper investigation of the stabilization effect of ferrocene (Table 1).

Although the molecular structures of **1**, **2**, **1O** and **3O** in the solid state did not show any strong intermolecular interactions, we investigated the presence of potential aggregates in solution with ^1H-DOSY NMR experiments. The diffusion properties

Table 1. ^{31}P NMR shifts, $^1J_{PH}$ couplings, MW_{dif} based on ^1H DOSY[a] and temperatures of disproportionation[b] for phosphines **1**–**4** and corresponding oxides.

Phosphine	**1**	**2**	**3**	**4**
δ_P [ppm]	−144.1	−129.3	−136.5	−137.4
$^1J_{PH}$ [Hz]	204	195	195	195
MW_{dif} [%]	+20	+13	+20	+14
Phosphine oxide	**1O**	**2O**	**3O**	**4O**
δ_P [ppm]	−1.1	9.6	5.9	7.8
$^1J_{PH}$ [Hz]	483	469	465	462
MW_{dif} [%]	+19	+9	+6	+9
T_{dis} [°C]	60–70	80–90	70–80	80–100

[a] Positive value of calculated MW_{dif} refers to a smaller MW in solution compared to the theoretical value for the monomer. [b] The intervals measured in toluene show the beginning and full disproportionation, respectively.

obtained by this method have been analyzed using standard software with external calibration curves (^{1}H-DOSY-ECC-MW estimation)[12] to derive the molecular weight of the compound in solution and its deviation from the formula weight MW_{dif} (Table 1). Our results confirmed the monomeric nature of all compounds in solution, within the expected error interval. Any stabilization of the compounds in solution by the formation of dimers or oligomers affecting the air-sensitivity therefore can be ruled out.

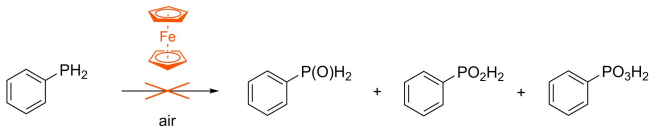
Given the exclusion of the stabilization through bond or molecular aggregation, we wondered whether ferrocene could provide intermolecular stabilization for the primary phosphine group.

Therefore, we stirred a chloroform solution of pyrophoric phenyl phosphine in air for 12 h (Scheme 3). A control experiment (without any added ferrocene) showed 32% phenyl phosphine in the mixture with phenyl phosphinic acid as a main oxidation product (65%). An identical experiment with 25 mol% of ferrocene did not show any oxidation with 100% of phenyl phosphine remaining unchanged in the solution.

In the following set of experiments, we compared the antioxidant effect in different solvents (Table 2). The intermolecular effect of ferrocene was demonstrated in all tested solvents, with notable efficacy observed in chlorinated ones. The significant oxidation in tetrahydrofuran can be related to the intermediate formation of peroxides in the solvent under aerobic conditions.

Our subsequent series of experiments aimed at comparing the antioxidant activities of various metallocene derivatives (Table 3). The activity of ferrocene (FcH) was found to be remarkable, even at a one percent concentration of the substance. Electron-rich derivatives, particularly decamethylferrocene (DmFc), demonstrated superior activity in comparison to electron-deficient compounds, while heavier metallocenes exhibited negligible performance.

In the next step, we chose ferrocene as readily accessible and thermodynamically stable complex, and decamethyl-ferrocene as the most active compound to explore the possible extension of the effect to other phosphines (Table 4). Oxidation of more reactive primary phosphines showed to be also inhibited and the effect was prominent for secondary phosphines as well. Regarding tertiary phosphines, we skipped the air-stable triphenylphosphine and focused on electronically rich and highly reactive ones. Still, the antioxidant effect was significant, however, even a dramatic increase in the amount of the added complex did not lead to full termination of their oxidation.



Scheme 3. The antioxidant effect of ferrocene on oxidation of phenyl phosphine in air.

Table 2. Effect of solvent on oxidation of phenyl phosphine in the presence of ferrocene.[a]

Solvents	Ferrocene [mol%]	$PhPH_2$ [%]	Ferrocene [mol%]	$PhPH_2$ [%]
$CHCl_3$	25	100	1	88
CH_2Cl_2	25	100	1	18
toluene	25	87	1	16
DMSO	25	86	1	30
MeCN	25	80	1	25
THF	25	10	1	4

[a] The 0.5 M solutions of $PhPH_2$ with ferrocene were prepared in a glovebox, stirred overnight in air followed by ^{31}P NMR analysis. The percentage values represent the amount of unoxidized phosphine remaining after the reaction time.

Table 3. Complex screening for oxidation of phenyl phosphine in air.[a]

Complex	Loading [mol%]	$PhPH_2$ [%]	Loading [mol%]	$PhPH_2$ [%]
ferrocene	5	98	1	88
ethylferrocene	5	96	1	92
1,1′-dimethylferrocene	5	100	1	40
1,1′-(*tert*-butyl)ferrocene	5	100	1	33
decamethylferrocene	5	100	1	100
1,1′-dibromoferrocene	5	20	1	22
1,1′-diacetylferrocene	5	86	1	26
ferrocenecarboxaldehyde	5	83	1	32
cobaltocene	5	14	1	23
ruthenocene	5	15	1	16

[a] The 0.5 M solutions of $PhPH_2$ in chloroform with different complexes were prepared in a glovebox, stirred 14 h in air followed by ^{31}P NMR analysis. The percentage values represent the amount of non-oxidized phosphine remaining after the reaction time.

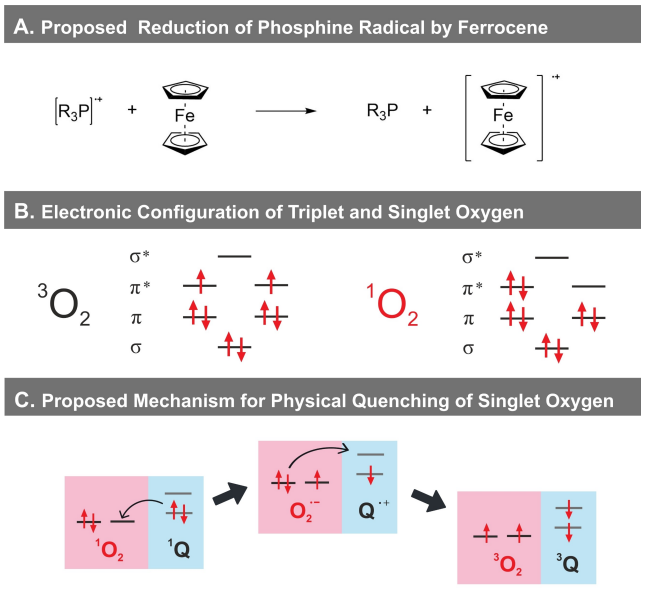
Table 4. Substrate screening for oxidation of phosphines. Control experiment = no addition of any complex, FcH = ferrocene, DmFc = decamethylferrocene.[a]

Experiment	Control	25 mol% FcH	5 mol% DmFc
Phosphine	[%]	[%]	[%]
$PhPH_2$	33	100	100
$BzPH_2$	0	48	100
$CyPH_2$	0	100	100
t-$BuPH_2$	0	81	93
Ph_2PH	0	98	100
$P(t\text{-}Bu)_3$	40	47	45 (97)[b]
PCy_3	0	72	75 (77)[b]

[a] The 0.5 M solutions of phosphine in chloroform with metallocene were prepared in a glovebox, stirred 14 h in air followed by ^{31}P NMR analysis. The percentage values represent the amount of non-oxidized phosphine remaining after the reaction time. [b] One molar equivalent of DmFc was added.

In an attempt to explain the observed antioxidant effect, we tested further hypotheses. Firstly, could ferrocene act as reductant and stop the phosphine oxidation by reducing an initially formed phosphine radical cation (compare Schemes 1A and 4A)?

To verify that, we were looking for traces of ferrocenium in the solution. Nevertheless, the UV-Vis spectrum of the solution after the reaction time did not exhibit any indications of ferrocenium. In other words, ferrocene is not consumed during the inhibition. Further, we decided to generate the phosphine radical of phenyl phosphine electrochemically. During CV measurements, we observed irreversible oxidation to the radical cation as known from the literature.[5a] Unfortunately, the addition of decamethyl-ferrocene to the solution did not lead to a reversible electrochemical pathway or quenching of the generated cation, under our experimental conditions. Thus, our attention shifted to the second reactant of the phosphine oxidation–oxygen.



Scheme 4. Proposed explanation for the intermolecular antioxidant activity of ferrocene in oxidation of phosphines. Q = physical quencher of singlet oxygen.[13]

Table 5. Quencher screening for the aerobic oxidation of phenyl phosphine.[a]

Quencher [25 mol%]	Fragment in phosphine	PhPH2 [%]
DABCO	–	100
β-carotene	–	95
2-naphthol	**I.**	100
1,1′-binaphthalene[b]	**II.**	91
anthracene[b]	**III.**	100
propionanilide	**IV.**	86
diethyl sulfide/ dimethyl disulfide/ 1,3,5-trithiane[b]	**V.**	≈10

[a] The 0.5 M solutions of $PhPH_2$ in chloroform with different quenchers were prepared in a glovebox, stirred 14 h in air followed by ^{31}P NMR analysis. The percentage values represent the amount of unoxidized phosphine remaining after the reaction time. [b] One molar equivalent was used.

Dioxygen is known to be a strong oxidant, but kinetically, in its triplet ground state, is fairly inert. Therefore, it can react only with radicals, or must be excited to its singlet state (Scheme 4B).[14] As singlet oxygen is also a stronger electron acceptor, it could be an initiator of a tandem radical reaction resulting in the known pyrophoric nature of primary phosphines. To support this second hypothesis, we replaced ferrocene in the oxidation of phenyl phosphine with known singlet oxygen quenchers (Scheme 4C). The crucial experiment involved 1,4-diazabicyclo[2.2.2]-octane (DABCO) as a known excellent physical singlet oxygen quencher,[15] but a poor free radical inhibitor[16] (Table 5). The experiment showed 100% of non-oxidized phosphine in the mixture. The result was confirmed also in the reaction with β-carotene as another known physical singlet oxygen quencher.[13]

It is well known that ferrocene is a good quencher of many excited states.[17] Furthermore, it is established that ferrocene is also a good quencher of singlet oxygen.[18] However, this finding seems somewhat overlooked in the current literature, despite its importance for prominent classes of compounds, such as ferrocene phosphines. For the latter a strongly antioxidant effect emerges from the presence of the ferrocene unit in the molecule. In line with our findings, the ferrocenyl moiety in **2** with an additional methylene spacer connecting the PH_2 unit is more electron rich and thus more protective than in **1** where the PH_2 is connected directly to the ferrocene.

While studying the structural design of known quenchers of singlet oxygen in the literature,[19] the striking similarity with the structures of the published air-stable primary phosphines (compounds **I.-V.** in Scheme 1D) caught our attention. Phenols,[20] polycyclic aromatic hydrocarbons,[21] nitrogen[22] and sulfur[23] compounds are known singlet oxygen quenchers. Thus, as before, we examined the structural fragments of phosphines **I.-V.** in oxidation of phenyl phosphine (Table 5). With a single exception, the antioxidant effect was readily apparent from the functionalities present in the molecules. On the contrary, sulfur compounds seemed to support, rather than inhibit, the oxidation. A possible explanation lies in the fact that sulfides have two different physical quenching mechanisms, where one of them contains a persulfoxide as an intermediate.[19]

Conclusions

In summary, we have demonstrated that the antioxidant effect of the ferrocene moiety on the autoxidation of primary phosphines is solvent dependent and increases with the electron density on the ferrocene moiety, but has no redox related grounds, for instance by reducing an intermediate phosphanyl radical cation. In contrast to previously proposed models explaining the air stability of primary phosphines, we have provided evidence that stabilization of the latter occurs on an intermolecular level

suggesting that the quenching of singlet oxygen is the decisive factor. In line with this, the structures of previously published air-stable primary phosphines also revealed the presence of singlet-oxygen quenchers, thus demonstrating the crucial role of singlet oxygen in the oxidation of phosphines.

Experimental Section

NMR studies, study of thermal disproportionation of primary phosphine oxides, precursors synthesis and all details about the characterization methods are presented in the Supporting Information.

CAUTION! Primary phosphines and their solutions are toxic, highly malodorous, and flammable or pyrophoric liquids as indicated in their Safety Data Sheets. Although the addition of a singlet oxygen quencher to their solution minimizes the chance of ignition, they should be handled only in a well-ventilated fume hood, away from all potential sources of ignition.

Synthesis of ferrocenylphosphine oxide (1O). In air, ferrocenylphosphine (260 mg, 1.00 mmol) was dissolved in a mixture of methanol and dichloromethane (10 mL of each), and the reaction flask, equipped with a stirring bar, was cooled in an ice bath. Hydrogen peroxide solution (1.0 mL of 35% aqueous solution, 10.3 mmol) was added for 3 min while stirring, and the resulting mixture was stirred and cooled for another 3 min. The excess of hydrogen peroxide was destroyed by slowly adding saturated aqueous sodium thiosulfate (10 mL). The mixture was transferred to a separatory funnel and diluted with dichloromethane (10 mL) and brine (10 mL). The organic phase was separated, and the aqueous residue was extracted with dichloromethane (10 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under a vacuum (***CAUTION!*** *The oxide* ***1O*** *easily sublimates*). The crude product was purified by flash column chromatography over silica gel using a dichloromethane-methanol mixture (gradient 2→15) as the eluent. Evaporation of the second yellow band afforded phosphine oxide **1O** as an orange solid. Yield: 150 mg, 64%. Crystal suitable for the structure determination was obtained by sublimating of the compound in a vacuum at 30 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, $^{1}J_{PH}$ = 483.1 Hz, 2H, PH_2), 4.57 (br s, 2H, C_5H_4), 4.54 (br s, 2H, C_5H_4), 4.31 (s, 5H, C_5H_5). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 72.6 (d, J_{PC} = 11 Hz, C_5H_4), 71.8 (d, J_{PC} = 15 Hz, C_5H_4), 69.5 (s, C_5H_5), 68.8 (d, $^{1}J_{PC}$ = 114 Hz, C_5H_4). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ −1.1 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ −1.1 (t, $^{1}J_{PH}$ = 483 Hz). ESI-MS: *m/z* 257 $[M+Na]^+$. Anal. calcd. (%) for $C_{10}H_{11}OFeP$ (234.0): C 51.33, H 4.74; found: C 51.59, H 4.73.

Synthesis of (ferrocenylethyl)phosphine (3). Under argon, trimethylchlorosilane (0.9 mL, 7.09 mmol) was slowly introduced to a suspension of $Li[AlH_4]$ (269 mg, 7.09 mmol) in dry THF (100 mL) while stirring and cooling on ice. The resulting mixture was stirred for 10 min before adding a solution of phosphonate **3R** (879 mg, 2.32 mmol in 100 mL of THF). After completing the addition, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 14 h. Then, the reaction flask was cooled in an ice bath, and methanol (20 mL) was added to terminate the reaction, before evaporating under vacuum. The residue was taken up with hexane (100 mL), and the extract was filtered and evaporated. The crude product was purified by column chromatography (silica gel, diethyl ether/hexane, gradient 20→50). Evaporation of the single orange band gave phosphine **3** as an orange solid. Yield: 470 mg (82%). The compound is known.[8g] ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.11 (s, 5H, C_5H_5), 4.08–4.07 (m, 2H, C_5H_4), 4.07–4.06 (m, 2H, C_5H_4), 2.72 (dm, $^{1}J_{PH}$ = 195.0 Hz, 2H. PH_2), 2.57–2.51 (m, 2H, CH_2), 1.74–1.67 (m, 2H, CH_2). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ −136.5 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ −136.5 (tm, $^{1}J_{PH}$ = 195 Hz).

Synthesis of (ferrocenylethyl)phosphine oxide (3O). In air, ferrocenylethylphosphine (197 mg, 0.80 mmol) was dissolved in a mixture of methanol (4 mL) and dichloromethane (10 mL), and the reaction flask, equipped with a stirring bar, was cooled in an ice bath. Hydrogen peroxide solution (0.5 mL of 30% aqueous solution, 4.40 mmol) was added for 3 min while stirring, and the resulting mixture was stirred and cooled for another 3 min. The excess of hydrogen peroxide was destroyed by slowly adding saturated aqueous sodium thiosulfate (10 mL) The mixture was transferred to a separatory funnel and diluted with dichloromethane (10 mL) and brine (10 mL). The organic phase was separated, and the aqueous residue was extracted with dichloromethane (10 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under a vacuum. The crude product was purified by flash column chromatography over silica gel using a dichloromethane-methanol mixture (gradient 2→15) as the eluent. Evaporation of the second yellow band afforded phosphine oxide **3O** as a yellow solid. Yield: 165 mg, 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (dt, $^{1}J_{PH}$ = 464.6 Hz, $^{3}J_{HH}$ = 3.9 Hz, 2H, PH_2), 4.12 (s, 5H, C_5H_5), 4.10 (br s, 4H, C_5H_4), 2.77–2.70 (m, 2H, CH_2), 2.23–2.15 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 86.4 (d, $^{3}J_{PC}$ = 15 Hz, C_5H_4), 68.8 (s, C_5H_5), 68.1 (s, C_5H_4), 67.9 (s, C_5H_4), 29.1 (d, $^{1}J_{PC}$ = 66 Hz, CH_2), 21.5 (d, $^{2}J_{PC}$ = 3 Hz, CH_2). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ 5.9 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ 5.9 (t, $^{1}J_{PH}$ = 465 Hz). ESI-MS: *m/z* 285 $[M+Na]^+$. Anal. calcd. (%) for $C_{12}H_{15}OFeP$ (262.1): C 55.00, H 5.77; found: C 55.37, H 5.97.

Synthesis of (ferrocenylpropyl)phosphine (4). Under argon, trimethyl-chlorosilane (0.57 mL, 4.50 mmol) was slowly introduced to a suspension of $Li[AlH_4]$ (171 mg, 4.50 mmol) in dry THF (15 mL) while stirring and cooling on ice. The resulting mixture was stirred for 10 min before adding a solution of phosphonate **4R** (0.588 g, 1.50 mmol in 15 mL of THF). After completing the addition, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 14 h. Then, the reaction flask was cooled in an ice bath, before adding methanol (20 mL) to terminate the reaction before evaporating under vacuum. The residue was taken up with dichloromethane (45 mL), filtered through a pad of celite, and evaporated. The crude product was purified by column chromatography (silica gel, hexane-diethyl ether, gradient 30→60). Evaporation of the single orange band gave phosphine **4** as an orange solid. Yield: 336 mg (86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.10 (s, 5H, C_5H_5), 4.05-4.04 (m, 4H, C_5H_4), 2.70 (dt, $^{1}J_{PH}$ = 195.2 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H, PH_2), 2.40 (t, J_{HH} = 7.7 Hz, 2H, CH_2), 1.75–1.68 (m, 2H, CH_2), 1.56–1.49 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 88.6 (s, C_5H_4), 68.6 (s, C_5H_5), 68.2 (s, C_5H_4), 67.3 (s, C_5H_4), 34.5 (d, J_{PC} = 3 Hz, CH_2), 30.6 (d, J_{PC} = 6 Hz, CH_2), 13.8 (d, J_{PC} = 8 Hz, CH_2). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ −137.4 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ −137.4 (t, $^{1}J_{PH}$ = 195 Hz). ESI-MS: *m/z* 260 $[M-e]^+$. Anal. calcd. (%) for $C_{13}H_{17}FeP$ (260.1): C 60.03, H 6.59; found: C 60.07, H 6.89.

Synthesis of (ferrocenylpropyl)phosphine oxide (4O). In air, (ferrocenylpropyl)phosphine (260 mg, 1.00 mmol) was dissolved in a mixture of methanol (10 mL) and dichloromethane (20 mL), and the reaction flask, equipped with a stirring bar, was cooled in an ice bath. Hydrogen peroxide solution (1.0 mL of 35% aqueous solution, 10.30 mmol) was added for 4 min while stirring, and the resulting mixture was stirred and cooled for another 10 min. The excess of hydrogen peroxide was destroyed by slowly adding saturated aqueous sodium thiosulfate (10 mL) The mixture was transferred to a separatory funnel and diluted with dichloromethane (30 mL) and brine (10 mL). The organic phase was separated, and the aqueous residue was extracted with dichloromethane (10 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under a vacuum. The crude product was purified by flash column chromatography over silica gel using a dichloromethane-

methanol mixture (gradient 2→20) as the eluent. Evaporation of the second orange band afforded phosphine oxide **4O** as a yellow solid. Yield: 270 mg, 98%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (dt, $^{1}J_{PH}$ = 461.9 Hz, $^{3}J_{HH}$ = 3.9 Hz, 2H, POH_2), 4.10 (s, 5H, C_5H_5), 4.08–4.06 (m, 4H, C_5H_4), 2.52 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2), 2.03–1.95 (m, 2H, CH_2), 1.87–1.78 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 87.1 (s, C_5H_4), 68.7 (s, C_5H_5), 68.3 (s, C_5H_4), 67.7 (s, C_5H_4), 30.5 (d, $^{2}J_{PC}$ = 15 Hz, CH_2), 27.0 (d, $^{1}J_{PC}$ = 66 Hz, CH_2), 23.0 (d, $^{3}J_{PC}$ = 3 Hz, CH_2). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ 7.8 (s). ^{31}P NMR (202 MHz, $CDCl_3$): δ 7.8 (tm, $^{1}J_{PH}$ = 462 Hz). ESI-MS: *m/z* 299 $[M+Na]^+$. Anal. calcd. (%) for $C_{13}H_{17}OFeP$ (276.0): C 56.55, H 6.21; found: C 56.53, H 6.28.

Supporting Information

The authors have cited an additional reference within the Supporting Information (Ref. [24]).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] a) L. A. Adrio, K. K. Hii, *Organometallic Chemistry, Vol. 35* (Eds.: I. J. S. Fairlamb, J. M. Lynam), **2009**, pp. 62–92; b) H. Guo, Y. C. Fan, Z. Sun, Y. Wu, O. Kwon, *Chem. Rev.* **2018**, *118*, 10049–10293; c) J. S. Greaves, A. M. S. Richards, W. Bains, P. B. Rimmer, H. Sagawa, D. L. Clements, S. Seager, J. J. Petkowski, C. Sousa-Silva, S. Ranjan, E. Drabek-Maunder, H. J. Fraser, A. Cartwright, I. Mueller-Wodarg, Z. Zhan, P. Friberg, I. Coulson, E. l. Lee, J. Hoge, *Nature Astronomy* **2021**, *5*, 655–664; d) E. Regulska, C. Romero-Nieto, *Materials Today Chemistry* **2021**, *22*, 100604.

[2] B. Stewart, A. Harriman, L. J. Higham, *Organometallic Chemistry, Vol. 38* (Eds.: I. J. S. Fairlamb, J. M. Lynam), The Royal Society of Chemistry, **2012**, pp. 36–47.

[3] a) S. A. Buckler, *J. Am. Chem. Soc.* **1962**, *84*, 3093–3097; b) S. Tojo, S. Yasui, M. Fujitsuka, T. Majima, *J. Org. Chem.* **2006**, *71*, 8227–8232; c) S. Yasui, S. Tojo, T. Majima, *J. Org. Chem.* **2005**, *70*, 1276–1280; d) H. R. Hudson, *The Chemistry of Organophosphorus Compounds*, 1st ed., Ed. F. R. Harrtley, John Wiley & Sons, **1990**, *1*, 438–349; e) G. Pandey, D. Pooranchand, U. T. Bhalerao, *Tetrahedron* **1991**, *47*, 1745–1752.

[4] a) R. Gao, D. G. Ho, T. Dong, D. Khuu, N. Franco, O. Sezer, M. Selke, *Org. Lett.* **2001**, *3*, 3719–3722; b) K. Nahm, Y. Li, J. D. Evanseck, K. N. Houk, C. S. Foote, *J. Am. Chem. Soc.* **1993**, *115*, 4879–4884; c) D. G. Ho, R. Gao, J. Celaje, H.-Y. Chung, M. Selke, *Science* **2003**, *302*, 259–262.

[5] a) L. J. Higham, *Phosphorus Compounds: Advanced Tools in Catalysis and Material Sciences* (Eds.: M. Peruzzini, L. Gonsalvi), Springer, Dordrecht, **2011**, pp. 1–19; b) R. M. Hiney, L. J. Higham, H. Müller-Bunz, D. G. Gilheany, *Angew. Chem. Int. Ed.* **2006**, *45*, 7248–7251; c) D. Yakhvarov, M. Caporali, L. Gonsalvi, S. Latypov, V. Mirabello, I. Rizvanov, O. Sinyashin, P. Stoppioni, M. Peruzzini, *Angew. Chem. Int. Ed.* **2011**, *50*, 5370–5373.

[6] a) O. Moncea, D. Poinsot, A. A. Fokin, P. R. Schreiner, J.-C. Hierso, *ChemCatChem* **2018**, *10*, 2915–2922; b) S. A. Buckler, M. Epstein, *Tetrahedron* **1962**, *18*, 1211–1219; c) S. A. Buckler, M. Epstein, *J. Am. Chem. Soc.* **1960**, *82*, 2076–2077.

[7] a) F. Dankert, M. Fischer, C. Hering-Junghans, *Dalton Trans.* **2022**, *51*, 11267–11276; b) M. Yoshifuji, K. Shibayama, K. Toyota, N. Inamoto, *Tetrahedron Lett.* **1983**, *24*, 4227–4228.

[8] a) A. Ficks, C. Sibbald, S. Ojo, R. W. Harrington, W. Clegg, L. J. Higham, *Synthesis* **2013**, *45*, 265–271; b) F. L. Laughlin, A. L. Rheingold, N. Deligonul, B. J. Laughlin, R. C. Smith, L. J. Higham, J. D. Protasiewicz, *Dalton Trans.* **2012**, *41*, 12016–12022; c) N. Pillarsetty, K. Raghuraman, C. L. Barnes, K. V. Katti, *J. Am. Chem. Soc.* **2005**, *127*, 331–336; d) K. V. Katti, H. Gali, C. J. Smith, D. E. Berning, *Acc. Chem. Res.* **1999**, *32*, 9–17; e) M. Brynda, M. Geoffroy, G. Bernardinelli, *Chem. Commun.* **1999**, 961–962; f) N. J. Goodwin, W. Henderson, B. K. Nicholson, *Chem. Commun.* **1997**, 31–32; g) W. Henderson, S. R. Alley, *J. Organomet. Chem.* **2002**, *656*, 120–128.

[9] J. T. Fleming, L. J. Higham, *Coord. Chem. Rev.* **2015**, *297–298*, 127–145.

[10] a) F. Horký, I. Císařová, P. Štěpnička, *Chem. Eur. J.* **2021**, *27*, 1282–1285; b) F. Horký, I. Císařová, P. Štěpnička, *Organometallics* **2021**, *40*, 427–441; c) P. Štěpnička, F. Horký, *Eur. J. Inorg. Chem.* **2022**, *2022*, e202200276.

[11] a) B. A. Surgenor, L. J. Taylor, A. Nordheider, A. M. Z. Slawin, K. S. Athukorala Arachchige, J. D. Woollins, P. Kilian, *RSC Adv.* **2016**, *6*, 5973–5976; b) C. Spang, F. T. Edelmann, M. Noltemeyer, H. W. Roesky, *Chem. Ber.* **1989**, *122*, 1247–1254.

[12] a) R. Neufeld, D. Stalke, *Chem. Sci.* **2015**, *6*, 3354–3364; b) S. Alvarez, *Dalton Trans.* **2013**, *42*, 8617–8636; c) S. Bachmann, R. Neufeld, M. Dzemski, D. Stalke, *Chem. Eur. J.* **2016**, *22*, 8462–8465; d) S. Bachmann, B. Gernert, D. Stalke, *Chem. Commun.* **2016**, *52*, 12861–12864.

[13] H. Tamura, H. Ishikita, *J. Phys. Chem. A* **2020**, *124*, 5081–5088.

[14] C. Bianchini, R. W. Zoellner, *Advances in Inorganic Chemistry, Vol. 44* (Ed.: A. G. Sykes), Academic Press, San Diego, **1996**, pp. 263–339.

[15] Y. K. Petit, C. Leypold, N. Mahne, E. Mourad, L. Schafzahl, C. Slugovc, S. M. Borisov, S. A. Freunberger, *Angew. Chem. Int. Ed.* **2019**, *58*, 6535–6539.

[16] a) J. A. Jackson, M. D. Newsham, C. Worsham, D. G. Nocera, *Chem. Mater.* **1996**, *8*, 558–564; b) C. Ouannes, T. Wilson, *J. Am. Chem. Soc.* **1968**, *90*, 6527–6528.

[17] S. Fery-Forgues, B. Delavaux-Nicot, *J. Photochem. Photobiol.* **2000**, *132*, 137–159.

[18] a) A. Farmilo, F. Wilkinson, *Photochem. Photobiol.* **1973**, *18*, 447–450; b) J. D. P. Hrdlovič, M. Karvaš, J. Durmis, *Chem. Zvesti* **1974**, *28*, 792–801.

[19] S. Beutner, B. Bloedorn, T. Hoffmann, H.-D. Martin, *Methods in Enzymology, Vol. 319*, Academic Press, San Diego, **2000**, pp. 226–241.

[20] R. Scurlock, M. Rougee, R. V. Bensasson, *Free Radic. Res. Commun.* **1990**, *8*, 251–258.

[21] P. R. Ogilby, M. Kristiansen, D. O. Mártire, R. D. Scurlock, V. L. Taylor, R. L. Clough, *Polymer Durability, Vol. 249*, American Chemical Society, **1996**, pp. 113–126.

[22] M. Hild, H.-D. Brauer, *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 1210–1216.

[23] E. L. Clennan, D. Wang, C. Clifton, M. F. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 9081–9082.

[24] a) G. R. Knox, P. L. Pauson, D. Willison, *Organometallics* **1992**, *11*, 2930–2933; b) C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453–457; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341; d) G. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8; e) R. P. Davies, L. Patel, A. J. P. White, *Inorg. Chem.* **2012**, *51*, 11594–11601; f) J. P. Lewtak, M. Landman, I. Fernández, J. C. Swarts, *Inorg. Chem.* **2016**, *55*, 2584–2596; g) U. Nagel, A. Bublewitz, *Chem. Ber.* **1992**, *125*, 1061–1072.

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