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Synthesis, Structure and Properties of a Five-Coordinate Oxophosphorus(V) *meso*-Triphenylcorrole

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Treatment of six-coordinate (5,10,15-triphenylcorrole)dihydroxyphosphorus(V) [P(TPC)(OH)$_2$] with trifluoroacetic acid (TFA) in CH_2Cl_2 for 30 min at room temperature followed by recrystallization gave stable five-coordinate (5,10,15-triphenylcorrole)oxophosphorus(V) [P(TPC)O] in quantitative yield. The formation of [P(TPC)O] from [P(TPC)(OH)$_2$] in the presence of TFA was also monitored by NMR, absorption and fluorescence spectroscopic titration studies. The structure of the isolated [P(TPC)O] was confirmed by X-ray crystallography. In [P(TPC)O], the corrole ring is distorted, and the P^V ion is displaced by 0.456 Å from the N_4 plane towards the axial oxygen atom. This is unlike six-coordinate (5,10,15-triphenylcorrole)dimethoxyphosphorus(V) [P(TPC)(OCH$_3$)$_2$], in which the P^V ion lies in the porphyrin plane. NMR, absorption and fluorescence spectroscopy and electrochemical studies indicate that [P(TPC)O] exhibits interesting and distinct properties, which differ from the six-coordinate [P(TPC)(OCH$_3$)$_2$]. Attempts to reduce the P^V complex [P(TPC)O] to its corresponding P^{III} complex by treating it with $LiAlH_4$ resulted in the formation of six-coordinate (5,10,15-triphenylcorrole)dihydridophosphorus(V) [P(TPC)H$_2$].

Introduction

Corroles are tetrapyrrolic macrocycles, which are closely related to porphyrins, but because corroles have one direct pyrrole–pyrrole bond, they have one carbon atom less in their outer periphery and contain an extra NH proton in their inner core compared to porphyrins.[1] Thus, corroles have a –3 charge in their deprotonated form and often lead to the stabilization of metal ions in high oxidation states[2] unlike porphyrins, which have a charge of –2 in their deprotonated form and stabilize metals in low oxidation states. Based on these features, one expects that corroles can complex with a large number of metal ions, however, the coordination chemistry of corroles is largely restricted to transition metals,[3] and there are only a few examples in the literature on metallocorroles containing main group elements.[4] Recently, Gross et al.[5] reviewed the coordination chemistry of corroles containing main group elements and discussed their synthesis, spectroscopy, electrochemistry and crystallography as well as their chemical reactivity and stability features. The most prominent features of the main-group-element-containing corrole complexes is their strong fluorescence behaviour with record high quantum yields as noted for Ga^{III} and Al^{III} corroles.[6] Recently, insertions of phosphorus into new porphyrinoids such as triazacorroles,[7] *N*-fused porphyrins,[8] *N*-fused telluraporphyrins,[9] an expanded isophlorin[10] or a triply fused [24]pentaphyrin have been carried out, and their structural and electronic properties were studied.[11] Even though the phosphorus ion is smaller than the usual metal ions and is potentially a good fit for the small cavity of corroles, there are only three reports on phosphorus corrole complexes.[12] Paolesse et al.[12a] reported the first five-coordinate P^V corrole complex of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole **2** (Scheme 1), which contains an axial –OH group as confirmed by X-ray analysis. Kadish, Vogel et al.[12b] reported the synthesis and electrochemical studies of a five-coordinate P=O complex of 2,3,7,8,12,13,17,18-octaethylcorrole (H$_3$OEC) **3** (Scheme 1) but the crystal structure was not reported. Gross et al.[12c] reported the synthesis of a six-coordinate P^V complex of 5,10,15-tris(pentafluorophenyl)corrole (**4**, Scheme 1). Except the above-mentioned reports, to the best of our knowledge, there are no other reports on P^V corroles until our recent report[13] on the synthesis of a series of six-coordinate P^V complexes of *meso*-triarylcorroles such as (5,10,15-triphenylcorrole)dihydroxyphosphorus(V) [P(TPC)(OH)$_2$] (**5**, Scheme 1). The crystal structure analysis of P^V complexes of *meso*-triarylcorroles supported six coordination of the P^V ion with two axial ligands. However, our NMR spectroscopic studies indicated the existence of some amount of the corresponding five-coordinate P^V corrole due to partial dissociation of the six-coordinate P^V

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[‡] Single-crystal X-ray structure analysis

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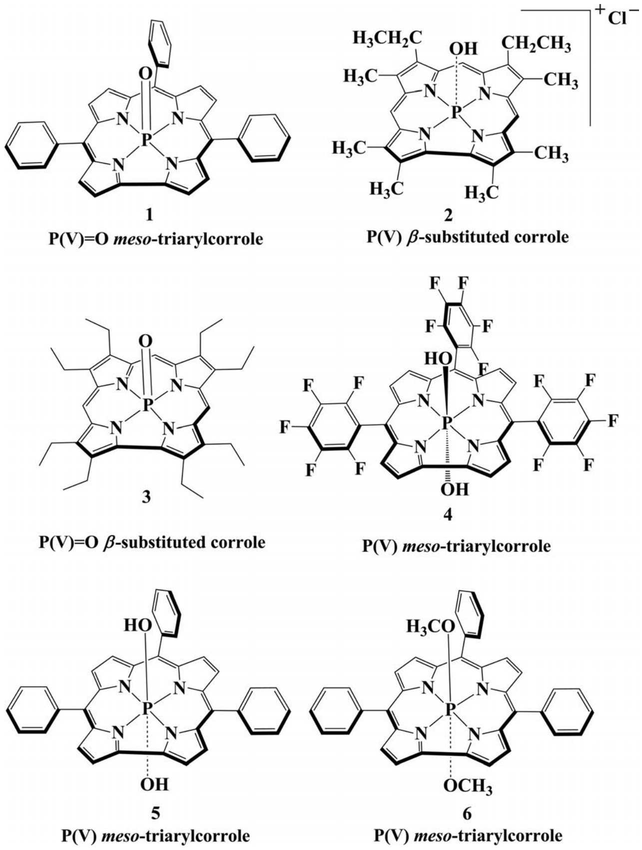
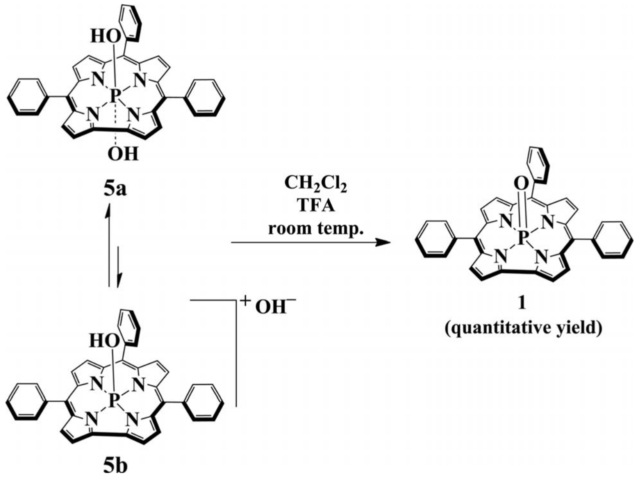
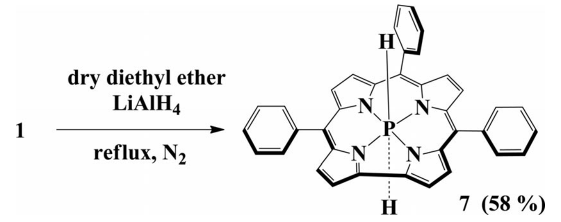
corrole complex upon standing for a long time in non-coordinating solvents. In coordinating solvents, such as CH_3OH, CH_3CN, dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), the P^V *meso*-triarylcorrole complexes exist only as six-coordinate complexes with two solvent molecules as axial ligands. For example, the six-coordinate complex (5,10,15-triphenylcorrole)dimethoxyphosphorus(V) $[P(TPC)(OCH_3)_2]$ (**6**, Scheme 1) was obtained as a pure stable compound by treating **5** with methanol followed by recrystallization. Attempts to isolate a pure five-coordinate P^V *meso*-triarylcorrole complex from the mixture of corresponding five- and six-coordinate P^V corroles were unsuccessful. The six-coordinate P^V complexes of *meso*-triarylcorroles, such as **6**, are strongly fluorescent with high quantum yields compared to those of weakly fluorescent P^V complexes of *meso*-tetraarylporphyrins.[14] Furthermore, the six-coordinate P^V *meso*-triarylcorroles exhibited very interesting absorption and electrochemical properties compared to those of six-coordinate P^V *meso*-tetraphenylporphyrins. As a five-coordinate P^V complex of *meso*-triarylcorrole had not been isolated to date, its properties remained elusive. Herein, we report the synthesis, structure, spectral and electrochemical properties of a stable five-coordinate neutral P^V=O complex of 5,10,15-triphenylcorrole **1** (Scheme 1). Compound **1** was prepared by treating $[P(TPC)(OH)_2]$ **5a**, which contains a small amount of the corresponding dissociated five-coordinate P^V complex **5b**, with trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature for 30 min followed by recrystallization (Scheme 2). The spectral and electrochemical properties of **1** are interesting and quite distinct from those of six-coordinate P^V corrole complex **6**. Our attempts to prepare a P^{III} *meso*-triarylcorrole complex by reducing **1** with $LiAlH_4$ resulted in the formation of only the six-coordinate P^V corrole complex $[P(TPC)H_2]$ (**7**) with two hydrides as axial ligands (Scheme 3).



Scheme 1. P^V corrole complexes **1**–**6**.



Scheme 2. Synthesis of **1**.



Scheme 3. Synthesis of **7**.

Results and Discussion

The six-coordinate P^V corrole complex **5a** was prepared by treating 5,10,15-triphenylcorrole (H_3TPC)[15] with $POCl_3$ in pyridine at reflux temperature for 30 min followed by column chromatographic purification as previously reported.[13] The six-coordinate compound **5a**, which contains hydroxy groups as axial ligands, is generally stable in the solid state, but in solution it shows partial dissociation to the corresponding five-coordinate P^V corrole complex **5b** leading to mixture of six- and five-coordinate complexes (Scheme 2). We assume that the five-coordinate complex formed here contains one axial –OH group. However, we cannot separate the five- and six-coordinate complexes by any separation technique. Hence, we prepared stable six-coordinate P^V corrole complexes such as **6** and characterized them by various techniques including X-ray crystallography.[13] In this work, the aim is to isolate a pure five-coordinate P^V *meso*-triarylcorrole complex and study its electronic and structural properties. We attempted various methods to convert the mixture of five- and six-coordinate complexes (**5a** and **5b**) to the five-coordinate P^V *meso*-triarylcorrole **1** in pure form. During the course of our investigations, we realized that the five-coordinate corrole **1** can be isolated by treating the mixture of six- and five-coordinate **5a** and **5b** with TFA at room temperature. The five-coordinate P^V=O complex of *meso*-triphenylcorrole **1** was synthesized by treating **5** with excess TFA in CH_2Cl_2 at room temperature for 30 min (Scheme 2). The reaction mixture changed from pink-violet to red as the reaction progressed. UV/Vis spectroscopy showed the disappearance of one of the Q-bands at 598 nm corresponding to a six-coordinate complex[13] and an increase in the intensity of the other two Q-bands at ca. 557 and ca. 522 nm indicating the formation of the five-coordinate P^V *meso*-triarylcorrole complex **1**. The Soret band also experienced a slight blue-shift on the formation of **1**. The solvent was removed with a rotary evaporator and the resultant solid was recrystallized from dry CH_2Cl_2/*n*-hexane to afford pure **1** as a pink-violet solid in quantitative yield. The composition of **1** was confirmed by HRMS (see S3 in the Supporting Information) and characterized by various spectroscopic techniques and X-ray crystallography. A comparison of the ^{1}H and ^{31}P NMR spectra of pure **6** and **1** is shown in Figure 1. It is clear from Figure 1 (a) that **6** exhibits four doublet of doublets at 8.78, 8.95. 9.03 and 9.38 ppm for eight β-pyrrole protons due to $^4J_{P,H}$ coupling in ^{1}H NMR spectroscopy. Upon formation of the five-coordinate P^V=O complex **1**, the sets of four β-pyrrole proton signals broadened and underwent a slight downfield shift to appear at 8.94, 9.22, 9.25 and 9.47 ppm (Table 1). The chemical shift of the phosphorus nucleus in ^{31}P NMR spectroscopy also gives information about the coordination number of the phosphorus centre, and detailed ^{31}P NMR studies on phosphorus derivatives of porphyrins, phthalocyanines and related macrocycles[16] indicate that six-coordinate phosphorus macrocyclic compounds generally show signals in the range –180 to –200 ppm, whereas five-coordinate compounds show signals in the range –90 to –110 ppm. As expected, the six-coordinate complex **6** showed a signal at –178 ppm, but **1** showed a signal at –98.5 ppm in ^{31}P NMR spectroscopy (part b of Figure 1 and Table 1), which supports a five-coordination environment around the phosphorus ion in **1**.

Furthermore, we followed the conversion of six-coordinate **5** to pure five-coordinate **1** by ^{1}H and ^{31}P NMR, absorption and fluorescence spectroscopic titration studies. The ^{1}H and ^{31}P NMR spectroscopic titration of six-coordinate **5a** containing a small amount of dissociated five-coordinate **5b** was carried out with an increasing amount of TFA in $CDCl_3$ (see S5 and S6, Supporting Information). In the ^{1}H NMR spectra, upon increasing the quantity of TFA added to **5** in $CDCl_3$, the more intense sets of four doublet of doublets at 8.80, 8.97, 9.05 and 9.26 ppm, which correspond to the eight β-pyrrole protons of the six-coordinate species **5a**, gradually disappear. At the same time, the other four less intense signals corresponding to the eight β-pyrrole protons of the five-coordinate corrole **5b** were gradually replaced by four unresolved broad sets of signals at 8.94, 9.22, 9.25 and 9.47 ppm (see S5, Supporting Information) due to the formation of the desired five-coordinate **1**. This is also clearly evident in the ^{31}P NMR spectra, which showed complete disappearance of a signal at ca. –191.4 ppm corresponding to the six-coordinate **5a** with the appearance of a signal at ca. –98.5 ppm due to the forma-

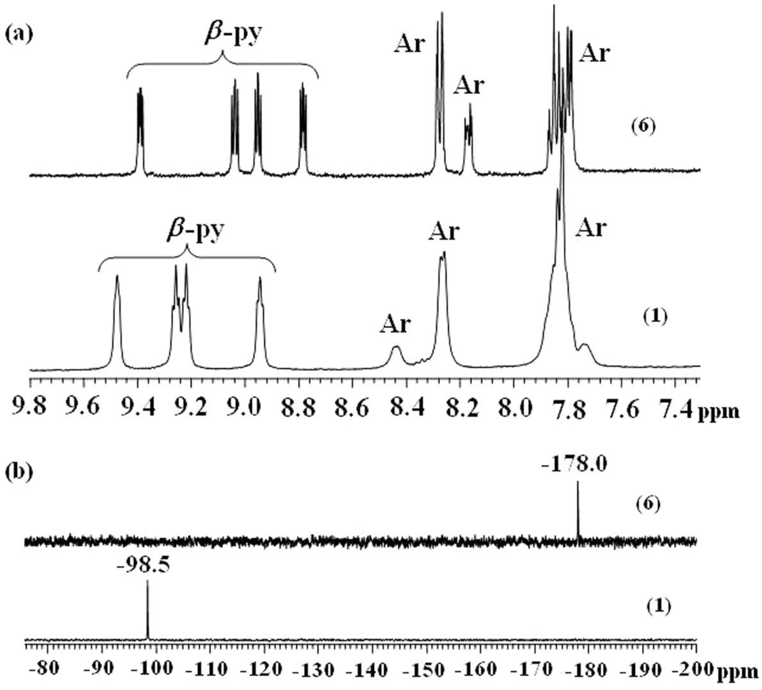


Figure 1. Comparison of (a) ^{1}H NMR spectra of **1** recorded in $CDCl_3$ and **6** recorded in CD_3OD and (b) ^{31}P NMR spectra of **1** recorded in $CDCl_3$ and **6** recorded in CD_3OD at room temperature.

Table 1. Selected ^{1}H, ^{31}P NMR, absorption, fluorescence, redox and crystallographic structural data for **1** and **6**.

	Six-coordinate **6**	Five-coordinate **1**
NMR[a]		
^{1}H NMR (β-pyrrole) [ppm]	9.38, 9.03, 8.95, 8.78	9.47, 9.25, 9.22, 8.94
^{31}P{^{1}H} NMR [ppm]	–178.0	–98.5
Absorption bands λ_{max} [nm], (logε)[b]	407 (5.41), 414 (5.36), 505 (sh), 521 (3.96), 547 (sh), 559 (4.13), 594 (4.60)	405 (5.40), 447 (3.74), 482 (sh), 522 (4.08), 557 (4.28)
Emission bands λ_{max} [nm][c]	600, 656 (sh)	568, 610 (sh)
Quantum yield (Φ)	0.44	0.27
Life time (τ) [ns]	3.01	1.61
Redox potentials [mV][c]	0.65, 1.11, 1.28, –1.48	0.64, 0.90
Crystal structure parameters		
Crystal system and space group	orthorhombic, *P*2$_1$	monoclinic, *P*2$_1$/*n*
Corrole ring geometry	almost planar	distorted
$\Delta_{4N}{}^{P}$ [d]	0.005	0.456
$\Delta_{23}{}^{P}$ [e]	0.033	0.478
P–O[f]	1.668, 1.663	1.500
P–N[g] (average)	1.83	1.80

[a] In CD_3OD for **6** and in $CDCl_3$ **1**. [b] In CH_3OH for **6** and CH_2Cl_2 for **1**. [c] In CH_3OH for **6** and in CH_2Cl_2 (in presence of trace amount of TFA) for **1**. [d] Displacement [Å] of phosphorus from the mean plane of the four pyrrole nitrogen atoms. [e] Displacement [Å] of phosphorus from the 23-atom mean plane of the corrole core. [f] Unit: Å. [g] Average value, unit: Å.

tion of the five-coordinate **1** (See S6, Supporting Information). Furthermore, in the ^{1}H NMR spectroscopic titration of **5**, we also observed the complete disappearance of the axial OH signal at –4.64 ppm due to formation of **1**. The absorption spectral titration studies also confirmed the conversion of six-coordinate **5** to five-coordinate **1** in the presence of TFA. Figure 2 shows the systematic changes in the absorption spectrum of **5** on addition of increasing amounts of TFA in CH_2Cl_2. Addition of TFA to **5** resulted in the gradual disappearance of the absorption band at 598 nm with a simultaneous increase in the absorption bands at 557 and 522 nm supporting the formation of five-coordinate **1**. Fluorescence spectral titration studies were carried out by adding TFA to **5** in CH_2Cl_2 and resulted in the disappearance of a fluorescence band at 607 nm corresponding to six-coordinate[13] **5** and the appearance of a new band at 568 nm due to the formation of five-coordinate **1** (Figure 3).

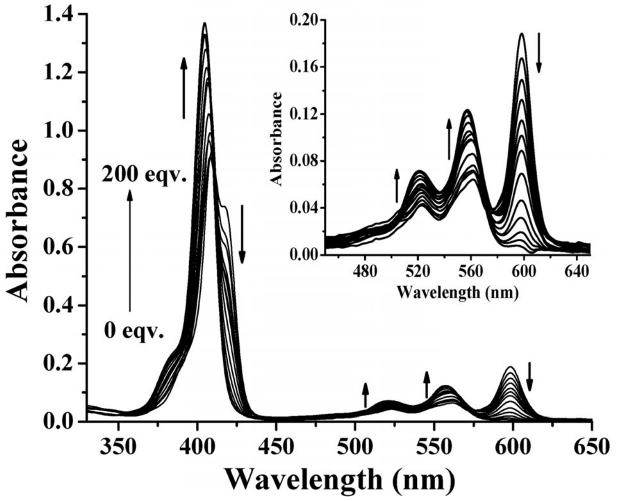


Figure 2. UV-titration of **5** with the addition of increasing amounts of trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature. An expansion of the Q-band region 450–645 nm is shown as inset.

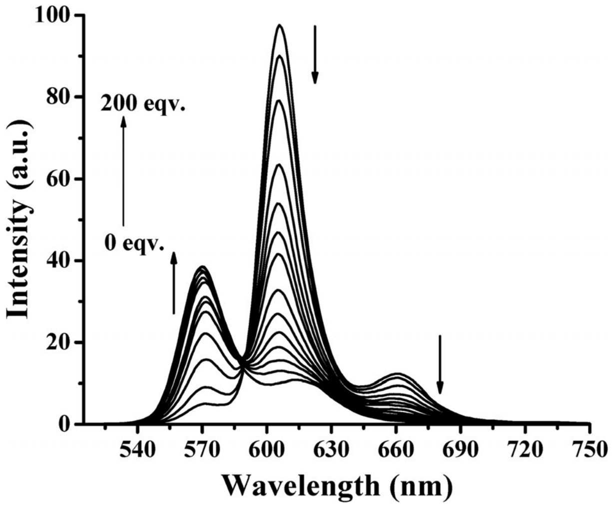


Figure 3. Fluorescence titration of **5** with the addition of increasing amounts of trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature.

The absorption, electrochemical and fluorescence properties of isolated five-coordinate **1** were studied and compared with those of six-coordinate **6**. The comparison of Q- and Soret band absorption spectra of **1** and **6** is shown in Figure 4 (a), and the data are presented in Table 1. As reported previously, six-coordinate **6** shows one strong Q-band at 594 nm and two or three other weak Q-bands in addition to one broad strong Soret band at 407 nm with a shoulder. However, five-coordinate **1** shows two moderately intense Q-bands at 552 and 557 nm and one sharp strong Soret band at 405 nm, which was slightly blueshifted compared to that of **6**. Interestingly, the strong Q-band at 594 nm for **6** is completely absent in the spectrum of **1**.

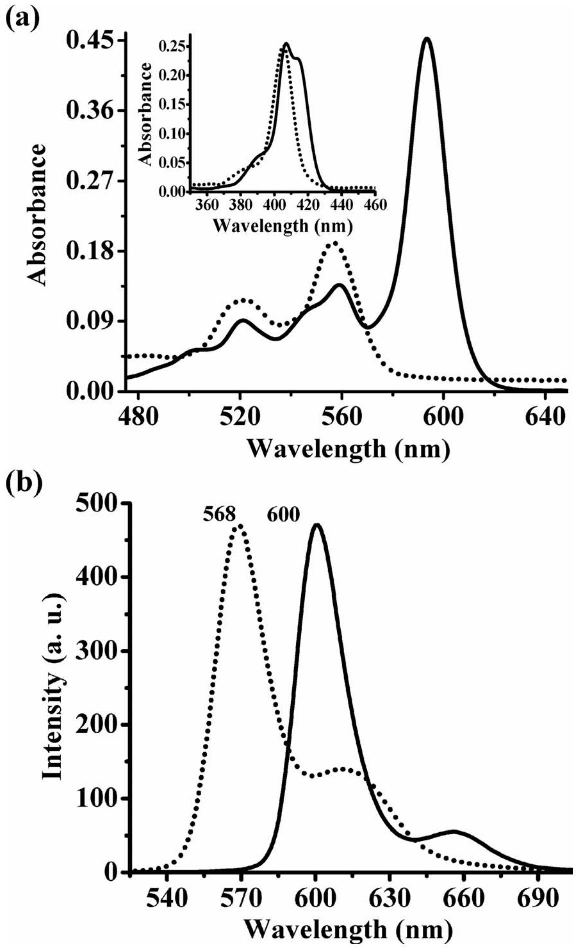


Figure 4. (a) Comparison of Q-band spectra of **1** (dotted line) in dry CH_2Cl_2 and **6** (solid line) in CH_3OH recorded at room temperature. The corresponding Soret band comparison is shown as inset. Concentrations of solution used for Soret band and Q-band measurements were 10^{-6} and 10^{-5} M, respectively. (b) Comparison of normalized fluorescence spectra of **1** (dotted line) in dry CH_2Cl_2 and **6** (solid line) in CH_3OH recorded at room temperature.

The electrochemical properties of **1** were studied by cyclic voltammetry and differential pulse voltammetry in dry CH_2Cl_2 in the presence of a trace amount of TFA by using a saturated calomel electrode (SCE) as the reference electrode and tetrabutylammonium perchlorate as the supporting electrolyte. Six-coordinate **6** showed one reversible oxidation, two irreversible oxidations and one reversible reduction. However, five-coordinate **1** showed one irreversible and one quasireversible oxidation but did not show any reduction (see S7, Supporting Information). The oxidation potentials of **1** were almost the same as that of **6** (Table 1), which indicates that **1** is as electron-rich as **6**.

The fluorescence properties of **1** and **6** were studied by both steady-state and time-resolved fluorescence techniques. A comparison of the steady-state fluorescence spectra of **1** and **6** is shown in Figure 4 (b). It is established that corroles containing main group elements are more fluorescent than transition metallocorroles, and Al^{III} and Ga^{III} metallocorroles are the brightest corrole complexes reported.[6] Our earlier fluorescence study on six coordinate P^V *meso*-triarylcorroles indicated that these are as brightly fluorescent as Al^{III} and Ga^{III} corroles and the quantum yields (Φ) and the singlet state lifetimes (τ) are in the range of 0.33–0.68 and 1.9–3.7 ns, respectively.[13] Five-coordinate **1** also showed a strong emission band at 568 nm, which is blueshifted compared to that of **6** (Figure 4, b). The quantum yield (Φ) of **1** is 0.27, which is slightly lower than that of **6**. The fluorescence decay of **1** was fitted to a single exponential curve (see S8, Supporting Information) and the singlet state lifetime (τ) is 1.61 ns. Thus, **1** is strongly fluorescent, and the fluorescence is diminished compared to that of **6**.

We attempted to prepare a P^{III} *meso*-triphenylcorrole complex by reducing **1** with $LiAlH_4$ in dry ether at reflux temperature for 20 min.[12b] As the reaction progressed, the reaction mixture changed from pink-red to green and finally to greenish violet. The crude compound was purified by alumina column chromatography, and HRMS (see S4 Supporting Information) and spectral analysis confirmed that the pure compound obtained was the six-coordinate dihydrido complex P^V *meso*-triphenylcorrole **7** and not the reduced P^{III} complex (Scheme 3). The ^1H NMR spectrum of **7** showed four doublets at 8.72, 8.93. 9.02 and 9.22 ppm corresponding to eight β-pyrrole protons and a doublet at –2.70 ppm corresponding to two axial hydride ligands, which supports the six-coordination environment around the P^V ion in **7** (Figure 5 and inset i). As the hydride ions are bound directly to the P^V ion, strong P–H coupling with a coupling constant J of ca. 935 Hz was observed, which is in agreement with the literature data.[12b] The proton-decoupled ^{31}P NMR spectrum of **7** (Figure 5, inset ii) showed a signal at –251 ppm consistent with six-coordination for the P^V ion. The absorption spectrum of **7** recorded in CH_2Cl_2 (see S9, Supporting Information) showed four Q-bands, which are bathochromically shifted compared to those of **6**. Furthermore, the Soret band in **7** is split and is bathochromically shifted compared to that of **6**. Electrochemical studies of **7** showed one reversible oxidation at 0.51 V, two irreversible oxidations at 1.06 and 1.18 V and one reversible reduction at 1.33 V (see S10, Supporting Information). Compared to six-coordinate **6**, compound **7** is

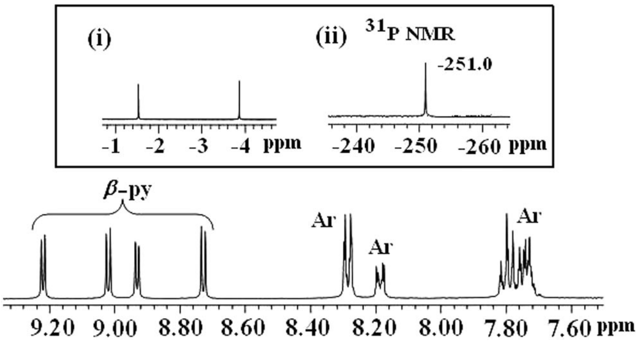


Figure 5. Partial ^1H NMR spectrum of **7** recorded in $CDCl_3$ at room temperature. The insets show (i) signal for the axial hydrogen atom coupled with the central phosphorus and (ii) ^{31}P NMR spectrum of **7**.

easier to oxidize and reduce. The decrease in the HOMO–LUMO gap from 2.13 V in **6** to 1.83 V in **7** is in agreement with the observed redshifts in the absorption bands of **7** compared to those of **6**. The fluorescence band of **7** is also significantly bathochromically shifted (ca. 100 nm) compared to that of **6** (see S11, Supporting Information). However, the fluorescence yield of **7** is reduced compared to that of **6**. Thus, **7** exhibited interesting spectral and electrochemical properties similar to other P^V *meso*-triarylcorroles.

Crystallographic Characterization

Further proof for the five-coordination of **1** was provided by single-crystal X-ray crystallography, and ORTEP plots of **1** are presented in Figure 6. Compound **1** was crystallized by the slow diffusion of *n*-hexane into a dry dichloromethane/chloroform mixture in the presence of a trace amount of TFA over one week. The structure of **1** obtained here is compared with our earlier reported six-coordinate P^V corrole **6**[13] and the previously reported five-coordinate P^V corrole **2**, which contains an axial –OH group.[12a] Unlike **6**, which crystallized in orthorhombic space group $P2_1$, **1** crystallized in the monoclinic space group $P2_1/n$. The crystal data and data collection parameters for **6** and **1** are summarized in Table 2. To the best of our knowledge, **1** is the first P^V=O complex of *meso*-triarylcorrole characterized by single-crystal X-ray analysis. In **1**, the five-coordinate phosphorus ion is 0.456 Å out of the mean corrole plane towards the axial oxygen atom (Table 1). This is similar to what is observed in the crystal structure of **2**, in which the central phosphorus ion was displaced by ca. 0.41 Å out of the mean corrole plane towards the axial –OH group. Such out of plane displacement of the central atom of metalloporphyrins[17] or metallocorroles[2,18] is commonly observed for five-coordinate complexes but not for six-coordinate complexes. For example, in six-coordinate **6**, the central phosphorus ion is almost in the mean plane defined by the four nitrogen atoms of the pyrrole rings. Similarly, in the case of the six-coordinate P^V complex of 5,10,15,20-tetraphenylporphyrin,[19] which is a close analogue of six-coordinate **6**, the central phosphorus atom has negligible out-of-plane displacement (ca. 0.09 Å) from the mean plane of the pyrrole nitrogen atoms. Furthermore, in **1**, the P=O bond length is 1.50 Å, which is slightly shorter than the P–OH bond length of ca. 1.532 Å observed in **2**. Similarly, the P–O bond lengths (P–O1 1.668, P–O2 1.663 Å) observed in **6** are somewhat longer than those in **1**. The P=O bond length in **1** is much shorter than the P–O bond lengths observed in other analogues such as six-coordinate P^V *meso*-tetraarylporphyrin complexes.[19] All of these observations support the hypothesis that the oxygen atom is bound to the central phosphorus ion through a double bond in **1**, unlike other P^V complexes of porphyrins and related macrocycles, in which the phosphorus ion is bound to the axial oxygen atom through a single bond. The four P–N bond lengths are not equivalent in **1**; the average P–N bond length (ca. 1.80 Å) is almost in the same range of the average P–N bond length (ca. 1.80 Å) found in **2** but is slightly shorter than the average P–N bond length (1.83 Å) observed in **6**. However, the average P–N bond length found in P^V corrole complexes **1**, **2** and **6** is somewhat shorter than that of analogous P^V porphyrin complexes (average P–N distance 1.89 Å)[19] as well as the average M–N distances found in metal complexes of *meso*-triaryl corroles.[3,4] Furthermore, the crystal structure of **1** revealed that the plane of the corrole ring is distorted and has a domelike structure. This is because, **1** is five coordinate and the central phosphorus ion is pulled towards the axial O atom causing a strain in the corrole skeleton, which results in distortion of the corrole ring. However, the corrole ring in six-coordinate **6** is more planar than that in free base corrole[20] as well as in other metallocorroles.[21] In free base corroles, such as 5,10,15-triphenylcorrole, the three inner NH protons cause steric crowding inside the corrole ring, which results in the distortion of the corrole macrocycle. On complexation with the small P^V ion, the strain imposed by the inner NH protons is released and the corrole ring becomes more planar in six-coordinate **6**. Furthermore, in

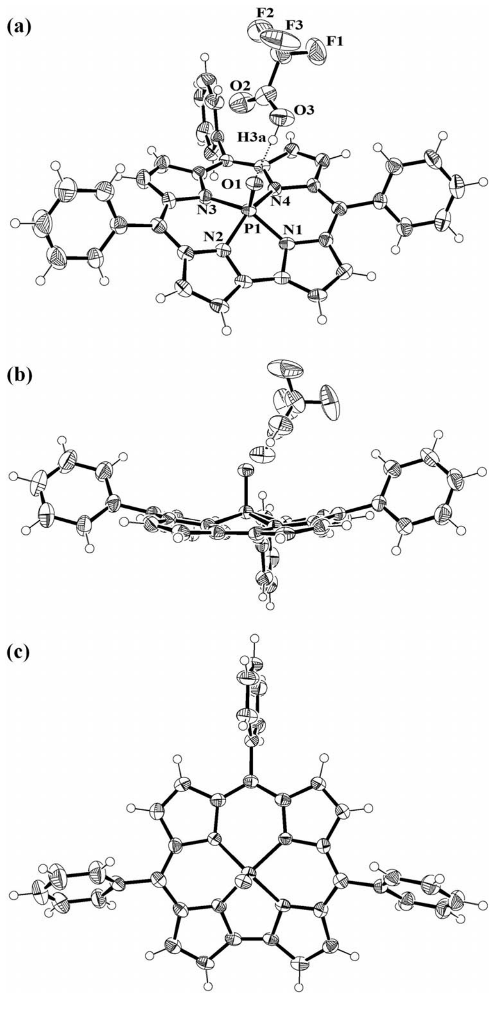


Figure 6. ORTEP diagram of **1**: a) perspective view, b) side view and c) top view (the TFA molecule is omitted for clarity). Ellipsoids are drawn at 50 % probability level.

six-coordinate **6**, the opposite *meso*-phenyl groups are oriented in a mutually opposite direction, whereas in five-coordinate **1**, the opposite phenyl groups are oriented in the same direction, and the average dihedral angles of the opposite *meso*-phenyl groups are ca. 55° and ca. 56°. The other *meso*-phenyl group is almost perpendicular (dihedral angle ca. 90°) to the mean plane of the corrole ring in both **1** and **6**. Interestingly, **1** was crystallized along with a TFA molecule, which is bound to the P=O oxygen atom through strong hydrogen bonding ($CF_3COO–H3a\cdots O1=P1$) as shown in Figure 6 (a). If the hydrogen bonding and the TFA molecule are not considered, the P^V corrole **1** is quite symmetric with a mirror plane going through the phosphorus ion, the *meso* carbon atom (C20) and the phenyl ring attached to the *meso* carbon atom (C20).

Table 2. Crystallographic data for compounds **1** and **6**.

	[P(TPC)O] (**1**)	[P(TPC)(OCH_3)$_2$] (**6**)
Molecular formula	$C_{39}H_{24}F_3N_4O_3P$	$C_{39}H_{29}N_4O_2P$
Fw	685.59	616.64
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1$
a [Å]	18.368(6)	8.3816(4)
b [Å]	7.992(3)	9.5266(6)
c [Å]	22.098(7)	37.694(2)
α [°]	90	90
β [°]	101.640(7)	90
γ [°]	90	90
V [Å^3]	3177.2(18)	3009.8(3)
Z	4	8
μ [mm^{-1}]	0.152	0.136
$D_{calcd.}$ [mg m^{-3}]	1.431	1.361
F(000)	1408	1288
2*θ* range [°]	1.88–25.03	3.28–25.00
e data (R_{int})	5600 [*R*(int) = 0.0862]	22842/5261
R_1, wR_2 [$I > 2\sigma(I)$]	0.0572, 0.1301	0.0445, 0.0844
R_1, wR_2 (all data)	0.1216, 0.1660	0.0684, 0.0895
GOF	0.994	0.929
Largest diff. peak/ hole [e Å^{-3}]	0.448/–0.629	0.241/–0.208

Conclusions

We isolated a stable five-coordinate P^V=O complex of *meso*-triphenylcorrole [P(TPC)O] by treating the six-coordinate P^V complex [P(TPC)(OH)$_2$] in CH_2Cl_2 with TFA at room temperature followed by recrystallization. The structure of [P(TPC)O] is unambiguously confirmed by X-ray crystallography. The corrole ring in [P(TPC)O] is slightly distorted and the phosphorus ion is placed above the corrole plane by 0.456 Å, unlike the six-coordinate complex [P(TPC)(OCH_3)$_2$], in which the corrole ring is planar and the P^V ion is almost in the N_4 plane of the corrole ring. The absorption, electrochemical and fluorescence properties of [P(TPC)O] are very interesting and distinct compared to those of six-coordinate P^V corrole complexes. [P(TPC)O] is highly fluorescent with a respectable quantum yield (*Φ*) and singlet state lifetime (*τ*). The treatment of [P(TPC)O] with $LiAlH_4$ resulted in the formation of six-coordinate (5,10,15-triphenylcorrole)dihydridophosphorus(V), which possesses interesting properties. Currently, the reactivity of five- and six-coordinate P^V *meso*-triarylcorroles complexes is under investigation.

Experimental Section

Chemicals: All general chemicals and solvents were procured from S. D. Fine Chemicals, India. Column chromatography was performed with silica gel and basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammonium perchlorate was purchased from Fluka and used without further purification. All NMR solvents were used as received. Solvents such as dichloromethane, tetrahydrofuran (THF) and *n*-hexane were purified and distilled by standard procedures.

Instrumentation: The ^1H and $^{31}P\{^1H\}$ NMR (*δ* in ppm) spectra were recorded with a Bruker AVANCE III 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for ^1H NMR spectra (residual proton; δ = 7.26 ppm) in $CDCl_3$ and 85% H_3PO_4 was used as an external reference for ^{31}P NMR spectra in $CDCl_3$ and CD_3OD. The HRMS spectra were recorded with a Q-Tof micromass spectrometer. Absorption and steady state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and PC1 Photon Counting Spectrofluorometer manufactured by ISS U.S.A., respectively. The fluorescence quantum yields (*Φ*) of P^V *meso*-triaryl corroles **1** and **6** were estimated from the emission and absorption spectra by the comparative method[22] using tetraphenylporphyrin (H_2TPP) as the standard (*Φ* = 0.11). The time-resolved fluorescence decay measurements were carried out at the magic angle by using a picosecond-diode-laser-based time-correlated single-photon-counting (TCSPC) fluorescence spectrometer from IBH, UK. All decay curves were fitted to single exponential functions by using IBH software. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were carried out with a BAS electrochemical system by utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. The experiments were performed in dry CH_3OH and CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

X-ray Crystallography: A single crystal of suitable size for X-ray diffractometry was selected under a microscope and mounted on the tip of a glass fibre, which was positioned on a copper pin. The X-ray data for **1** was collected with a Bruker Kappa CCD diffractometer, employing graphite-monochromated Mo-K_α radiation at 200 K and the *θ*–2*θ* scan mode. The space group for **1** was determined on the basis of systematic absences and intensity statistics, and the structure of **1** was solved by direct methods using SIR92 or SIR97 and refined with SHELXL-97.[23] An empirical absorption correction by multiscans was applied. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. Selected crystallographic data for **1** are given in Table 2.

CCDC-870321 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Synthesis: Free base *meso*-5,10,15-triphenylcorrole (H_3TPC) was synthesized by following a literature method.[15] The phosphorus derivatives **5** and **6** of corroles were synthesized as previously reported.[13]

Compound 1: To a dichloromethane (50 mL) solution of (5,10,15-triphenylcorrole)dihydroxyphosphorus(V) (**5**) (100 mg, 0.169 mmol), TFA (130 µL, 1.696 mmol) was added dropwise, and the reaction mixture was stirred for 30 min in air. The deep pink-violet solution immediately turned red. The progress of the reaction was followed by TLC analysis and absorption spectroscopy. After completion of the reaction, the solvent was evaporated under reduced pressure with a rotary evaporator. The crude solid was recrystallized from dry CH_2Cl_2/dry *n*-hexane and afforded a purple-red solid in quantitative yield (95 mg, 0.166 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (br., 2 H, β-pyrrole H), 9.25 (br., 2 H, β-pyrrole H), 9.22 (br., 2 H, β-pyrrole H), 8.94 (br., 2 H, β-pyrrole H), 8.43 (br., 1 H, Ar), 8.25–8.27 (br. m, 4 H, Ar), 7.73–7.85 (br. m, 10 H, Ar) ppm. ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$): δ = –98.5 ppm. UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 405 (5.40), 447 (3.74), 482 (sh), 522 (4.08), 557 (4.28) nm. HRMS: m/z = 571.1688 [M + 1]$^+$. $C_{37}H_{23}N_4OP\cdot CF_3COOH$: calcd. C 68.36, H 3.50, N 8.18; found C 68.59, H 3.25, N 8.57.

Compound 7: To a stirred dry diethyl ether solution (80 mL) of **1** (100 mg, 0.175 mmol), $LiAlH_4$ (67 mg, 1.75 mmol) was added under a nitrogen atmosphere. The reaction mixture was heated to reflux for 20 min under a nitrogen atmosphere. As the reaction progressed, the reaction mixture changed from pink-red to green and finally to greenish violet. The excess $LiAlH_4$ was quenched by adding methanol and water to the reaction mixture at low temperature. The reaction mixture was filtered, and the filtrate was evaporated with a rotary evaporator under reduced pressure. The crude solid was loaded on a basic alumina column and the desired first greenish-violet band was collected by using dichloromethane/petroleum ether (7:3). The compound was recrystallized from dichloromethane/*n*-hexane and afforded pure crystalline **7** as a dark violet solid in 58% yield (57 mg, 0.102 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 [d, $^3J_{H,H}$ = 4.24 Hz, 2 H, β-pyrrole H], 9.02 [d, $^3J_{H,H}$ = 4.84 Hz, 2 H, β-pyrrole H], 8.93 [d, $^3J_{H,H}$ = 4.16 Hz, 2 H, β-pyrrole H], 8.73 [d, $^3J_{H,H}$ = 4.80 Hz, 2 H, β-pyrrole H], 8.27–8.29 (m, 4 H, Ar), 8.17–8.20 (m, 2 H, Ar), 7.72–7.81 (m, 9 H, Ar), –2.70 [d, $J_{P,H}$ = 934.94 Hz, 2 H, axial H] ppm. ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$): δ = –251.01 ppm. UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (log ε) = 320 (br., 4.37), 422 (sh), 431 (4.97), 456 (5.08), 542 (br., 3.72), 588 (3.55), 635 (br., 3.96), 689 (4.59) nm. HRMS: m/z = 556.1819 [M]$^+$. $C_{37}H_{25}N_4P$ (556.61): calcd. C 79.77, H 4.49, N 10.06; found C 79.35, H 4.15, N 10.34.

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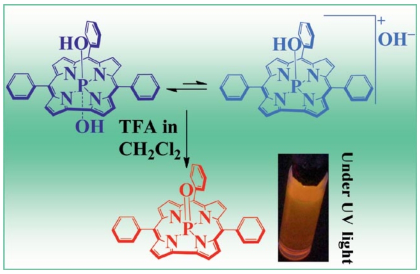
Phosphorus complexes

A stable five-coordinate P^V=O complex of *meso*-triphenylcorrole was isolated and structurally characterized, and its properties were studied.



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Synthesis, Structure and Properties of a Five-Coordinate Oxophosphorus(V) *meso*-Triphenylcorrole

Keywords: Fluorescence / Phosphorus / Coordination modes / Corroles

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