Copper Complexes of 1,4-Naphthoquinone Containing Thiosemicarbazide and Triphenylphosphine Oxide Moieties; Synthesis and Identification by NMR, IR, Mass, UV Spectra, and DFT Calculations

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ABSTRACT: New 1,4-naphthoquinone derived by triphenylphosphanylidene (Ph₃P) and N-substituted-hydrazine-1-carbothioamides were obtained during a one-pot reaction of 2,3-dichloro-1,4-naphthoquinone with thiosemicarbazides, Ph₃P and in the presence of triethyl amine (Et₃N) as a catalyst. The structure of the ligands was established by ESI, IR, and NMR spectra, in addition to elemental analyses and X-ray structure analysis. On subjecting the newly prepared ligands with CuCl₂ and Ph₃P, autoxidation occurs, and (E)-(2-(1,4-dioxo-3-(triphenylphosphanylidene)-3,4-dihydropyrene-2(1H)-ylidene)carbamothioyl)-hydrazinyl)-((triphenylphosphanyl)oxy)copper derivatives were formed in very good yields. The structure of the obtained complexes was proved by ESI, IR, NMR, and UV spectra, in addition to elemental analyses and theoretical calculations.

1. INTRODUCTION

Natural hydroxy derivatives of 1,4-naphthoquinone lawsone and juglone with hydroxyl groups in the α- and β-positions of the naphthalene core form salts and complexes with cations of various metals and are used as dyes.¹ Protein binding, DNA binding/cleavage, and in vitro cytotoxicity studies of 2-((3-(dimethylamino)-propyl)amino)naphthalene-1,4-dione and its four coordinated M(II) complexes [M(II) = Co(II), Cu(II), Ni(II), and Zn(II)] have been investigated. The complexes demonstrated a comparable in vitro cytotoxic activity against two human cancer cell lines (MCF-7 and A-549) with cisplatin. AO/EB and DAPI staining studies suggest an apoptotic mode of cell death in these cancer cells, with the compounds under investigation.² A series of nine Ru¹¹ arene complexes bearing tridentate naphthoquinone-based N,O,O-ligands were synthesized and characterized. The cytotoxic profile exhibited much higher cytotoxicity in SW480 colon cancer cells than in the broad chemos- (incl. platinum-) sensitive CH1/PA-1 teratocarcinoma cells. This activity pattern, reduced or slightly enhanced ROS generation, and the lack of DNA interactions indicate a mode of action different from established or previously investigated classes of metallodrugs.³

The reactions of 1,4-naphthoquinone with triphenylphosphine (Ph₃P), derivatives of phosphonium betaines derived from hexafluoro-1,4-naphthoquinone: (triphenyl-[5,6,7,8-tetrafluoro-1-oxido-4-oxo-3-(phenylimino)-3,4-dihydro-naphthalen-2-yl]phosphonium) 3 (Scheme 1), were obtained.⁴ The reaction was explained as due to the formation of intermediate 2 (Scheme 1). Depending upon reaction conditions, it was reported that Ph₃P reacted with p-chloranil (4) to produce either Zwitter salts 5 or 6 (Scheme 1). However, in aqueous alcoholic medium, 3-(triphenylphosphanylidene)naphthalene-1,2,4(3H)-trione (8)⁶ was obtained from the reaction of 2,3-dichloro-1,4-naphthoquinone (7) with Ph₃P (Scheme 1).

In the same manner, bisphosphonium salt containing a 1,4-dihydroxynaphthyl-substituted moiety was synthesized in high yield by the reaction of 2-methyl-1,4-naphthoquinone with three equivalents of Ph₃P and hydrogen bromide.⁷ Metal-free synthesis of aryldihydropyrophosphonium bromides by the reaction of Ph₃P with ary bromides in refluxing phenol was developed.⁸ With the high reactivity of naphthoquinones, 2,3-

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of 21 h, the main product was a bright red precipitate. However, when an ethanolic solution of 10 product, bis-(-nucleophiles and substituted one or both chlorine atoms.

It was found that the reaction of 7 with p-nitrobenzhydrazide (9) in 1:2 or 2:1 ratio in DMF gave only the disubstituted product, bis-(p-nitrobenzhydrazino)-1,4-naphthoquinone (10). However, when an ethanolic solution of 7 and 9 was refluxed for 21 h, the main product was a bright red precipitate of 11 (Scheme 2).

Scheme 2. Nucleophilic Addition of Aroylhydrazide 9 to Compound 7

On the basis that triphenylphosphine oxide (Ph₃P==O) can form facile complexes with some metal salts, Hergueta et al. reported the facile removal by complexation with CaBr₂, with Ph₃P==O in ethereal solvents or toluene. The resulting insoluble precipitated complex was easily eliminated from the crude reaction mixtures in high yields by filtration without the need for purification by column chromatography.

Copper(I) and silver(I) chloride complexes containing Ph₃P and 4-phenyl-thiosemicarbazide (4-PTSC) ligands were prepared and structurally analyzed, namely, [CuCl(4-PTSC)(Ph₃P)₂] (12) and [AgCl(4-PTSC)(Ph₃P)₂]CH₃CN. Both compounds exhibit a distorted tetrahedral metal coordination environment with two P atoms from two PPh₃ groups. On the basis that triphenylphosphine oxide (Ph₃P=O) can form facile complexes with some metal salts, Hergueta et al. reported the facile removal by complexation toward CuCl

2. RESULTS AND DISCUSSION

Thiosemicarbazones 14a-f were prepared by reacting substituted isothiocyanates 13a-f with hydrazine in ethanol as a solvent. Upon mixing equimolar amounts of 14a-f with 2,3-dichloro-1,4-naphthoquinone (7), Ph₃P, and in the presence of Et₃N as a catalyst and acetonitrile as a solvent, triphenylphosphine-yldiene-3,4-dihydronaphthalen-2(1H)-yldene)-N-substituted-hydrazine-1-carbothioamides were then subjected to complexation toward CuCl₂ and Ph₃P. The stability of these complexes was discussed using a plethora of quantum mechanical calculations and by executing Hirshfeld surface (HS) analysis.

The reactions between [CuCl₂(Ph₃P)₂] and 3,3-diphenyl-1-(2,4-dichlorobenzoyl)thiourea, 3,3-diisobutyl-1-(2,4-dichlorobenzoyl)thiourea, or 3,3-diethyl-1-(2,4-dichlorobenzoyl)thiourea in benzene gave four-coordinated tetrahedral copper(I) complexes of the type [CuCl₂(HL)(Ph₃P)₂] [HL = 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)-thiourea derivatives].

Previously, we reacted thiosemicarbazones derived from 2-quinolone with Cu(I), Cu(II), and Ni(II) salts. Mono-dentate Cu(I) quinolyl-substituted ligands were observed, whereas Ni(II) and Cu(II) gave bidentate-thiosemicarbazone derived by 2-quinolones. Subsequently, molecular docking was used to evaluate each analog’s binding affinity and the inhibition constant (kᵢ) to the RdRp complex of SARS-CoV-2. We also synthesized a series of paracyclophane-substituted thiosemicarbazones, thiocarbazones, hydrazones, and thioureas to study their complexation capability toward copper (I) and Cu (II) salts. Tridendate and bidentate of the aforesaid paracyclophane-substituted ligands were observed. Thiosemicarbazonyl, hydrazonyl, and thioarey paracyclophane derivatives formed with Cu(I) and Cu(II) salt tridentate and bidentate structures, whereas no complexes were observed for the prepared thiocarbasone derivatives.

Copper complexes have numerous properties, including proteasome activity inhibitors, DNA intercalation, and anticancer chelators. They can also increase the activity of the ligand itself. For example, 4-cyclohexyl-3-(4-nitrophenyl)-methyl-1,2,4-triazolin-5-thione has no activity against some selected bacteria, but after obtaining the metal(II) complex, the activity increases to a mild score.

From this, we here aim to investigate the reaction of 2,3-dichloro-1,4-naphthoquinone (7) together with thiosemicarbazides and Ph₃P to achieve the expected bi-nucleophilic substituted naphthoquinone. The newly obtained triphenylphosphino-yldiene-3,4-dihydronaphthalen-2(1H)-yldene)-N-substituted-hydrazine-1-carbothioamides were then subjected to complexation toward CuCl₂ and Ph₃P. The stability of these complexes was discussed using a plethora of quantum mechanical calculations and by executing Hirshfeld surface (HS) analysis.
protons at $\delta_H = 13.04$ (s, 1H, NH$_1$) and at 6.85 (s, 1H, NH$_2$). The benzyl-CH$_2$ resonated as a multiplet, in the $^1$H NMR spectrum, at $\delta_H = 4.38$−4.20. The $^{13}$C NMR spectrum showed the carbonyl carbon signals at $\delta_C = 177.2$ and 176.3, whereas the C=S and benzylic-CH$_2$ carbon signals appeared at $\delta_C = 162.8$ and 46.9 ppm, respectively. IR spectroscopy revealed the NH-stretching, C=O, and C=S groups at $\tilde{\nu} = 3340$−3055, 1153, and 988 cm$^{-1}$, respectively. X-ray structure analysis confirmed the structure of 15c, as shown in Figure 2.

Mass spectroscopy of 15f revealed $[M + H]^+$ at $m/z = 564$ (100), whereas the molecular ion peak appeared at $m/z = 563$ (30%). HRMS confirmed $[M + H]^+$ of compound 15f as C$_{33}$H$_{31}$N$_3$O$_2$P$_1$32S$_1$. The $^1$H NMR spectrum showed the two NH protons at $\delta_H = 13.18$ and 6.74. In the $^1$H NMR spectrum, the butyl protons resonated as a double-doublet ($J = 7.7$, 1.5 Hz, 2H) and three multiplets at $\delta_H = 3.58$, 1.60−1.49, 1.35−1.26, and 1.02−0.99 ppm, respectively. The $^{13}$C NMR spectrum showed the carbonyl carbon signals at $\delta_C = 186.1$ and 185.9, whereas C=S resonated at 178.4 ppm. The butyl carbon signals resonated in the $^{13}$C NMR spectrum at $\delta_C = 44.6$, 30.4, 20.1, and 14.0 ppm. IR spectroscopy displayed the NH-stretching at $\tilde{\nu} = 3340$−3053 (w, NH), whereas the two carbonyl groups and C=N appeared at $\tilde{\nu} = 1586$, 1521, and 1434, respectively. Besides, the C=P and the C=S groups appeared as strong bands in the IR spectra at $\tilde{\nu} = 1170$ and 992 cm$^{-1}$, respectively. The structure of 15f was confirmed by X-ray structural analysis, as shown in Figure 3.

In the crystal structures of 15c and 15f, are the bond distances and angles in the expected range with a slight delocalization of the $\pi$-electron in the thiosemicarbazide moiety (see cif-file). The thiosemicarbazide and 1,4-naphthoquinone moieties are coplanar.

The mechanism describes that the formation of 15a-f is based upon the addition of Ph$_3$P to C-1 (or C-2) in 7 to give the Zwiterion 17, which would be in resonance with the intermediate 18 (Scheme 4). The addition of 14a-f in the presence of Et$_3$N would then accompany the elimination of a molecule of HCl and another of Ph$_3$P to give 19a-f (Scheme 4). Subsequently, the extruded Ph$_3$P would again add to halogenated intermediates 19a-f to produce salts 20a-f (Scheme 4). Finally, a molecule of Et$_3$N would facilitate the formation of 20a-f via the elimination of a molecule of triethylammonium hydrochloride.

Figure 2. Molecular structure of compound 15c (displacement parameters are drawn at 50% probability level). Selected bond distances [Å] and angles [°]: C2−N9 1.3088(16), N9−N10 1.3674(14), N10−C11 1.3546(17), C11−S11 1.6775(13), C11−N12 1.3297(17), N12−C13 1.4557(17); C2−N9 N10 119.45(10), N9−N10−C11 119.65(10), C11−S11 N10 119.43(10), C11−N11 119.43(10), N10−C11−N12 116.90(11), C11−N12−C13 122.64(11).
together with a Ph₃PO molecule. Elemental analyses of compounds 16a-f are shown in Table 2.

2.2. Assignment by IR Spectra. The significant bands in infrared spectra for both ligands 15a-f and their metal complexes 16a-f are represented in Table 3. The symmetrical stretching of NH bands for compounds 16a-f was absorbed in the region at their expected region of IR spectra. The shift in functional groups from the ligands to the corresponding complexes supported the chelating process. Coordination occurred via N-2 and the oxygen atom of Ph₃P. The C=S stretching gave slight shifts in the case of a comparison between 15a-f and 16a-f. Most indicative is the new appearance of P=O, Cu–N, and Cu–O bands during the comparison between 15a-f and 16a-f. For example, IR spectroscopy of 15a showed the following bands at \( \nu = 3345, 3052 \) for NH stretching, 1188 (as a strong band) for C=S, and 993 (as a strong band) \( \mathrm{cm}^{-1} \) for s, Cu=S. In the case of 16a, the NH stretching was absorbed as a weak band at \( \nu = 3054 \), whereas at \( \nu = 1178 \), as a strong band for the C=O group. New bands were noted at \( \nu = 1019 \) (m, P=O), 536 (s, Cu–N), and 457 \( \mathrm{cm}^{-1} \) (s, Cu–O). Similar values of the previous three groups were previously reported. \(^{24,25}\) The same trend was also observed in all compounds 16b-f (Table 2).

2.3. Assignment of the Complexes 16a-f by NMR Spectra. Together with the elemental analyses, mass, and IR spectra, the chemical shift in NMR spectra, indicating the complexation process of 15a-f with Cu(II) to form 16a-f, as shown in Table 4. As it is known that although most NMR measurements are conducted on diamagnetic compounds, paramagnetic samples are also amenable to analysis and give rise to special effects indicated by a wide chemical shift range and broadened signals. \(^{26,27}\) However, several papers reported the use of the Cu(II) complex with Ph₃P of the composition CuCl₂(Ph₃P)$_2$. \(^{28–30}\) The previous studies showed that the oxidation state of II cannot be stabilized for copper in the presence of such a reducing ligand like Ph₃P. Therefore, Cu(II) is converted into Cu(I) during complexation with Ph₃P and compounds 15a-f. We here note that NMR spectra could be distinguished, and there are remarkable shifts in some values of the chemical shifts (\( \delta \)) of $^1$H NMR and $^{13}$C NMR spectra of compound 15a, as an example, compared with its complex 16a. In the $^1$H NMR spectrum, NH-2 resonated at \( \delta = 12.90 \), whereas NH-1 appeared at \( \delta = 5.77 \). The ethyl protons appeared as a quartet at \( \delta = 5.19 \) for CH$_2$ethyl, whereas a triplet at \( \delta = 6.42 \) ppm (\( J = 7.1 \) Hz). In the case of 16a (Table 4), the $^1$H NMR spectrum of only NH-1 at \( \delta = 5.49 \), whereas N-2 didn’t reveal any proton. The ethyl protons appeared as a quartet at \( \delta = 4.05 \) (\( J = 7.1 \) Hz) and a triplet at \( \delta = 1.20 \) ppm.

Interestingly, the reaction of equal equivalents of compounds 15a-f with Ph₃P and CuCl₂·2H$_2$O in ethanol at rt and for 1–3 d produced the Cu-complexes 16a-f (Scheme 5). Based on IR, $^1$H NMR, and mass spectra, together with elemental analysis, the NH-3 proton of the thiosemicarbazone moiety, in 15a-f, was eliminated, and aerial oxidation occurred, as shown in Scheme 5.

Reagents and conditions: 15a-f (1.00 equiv), CuCl₂·2H$_2$O (1.00 equiv) and Ph₃P (1.00 equiv) in absolute EtOH (40 mL), room temperature (2–4 h). Column chromatography (CC) using EtOAc/hexane (5:1).

2.1. Assignment of the Ligands 15a-f and Their Cu-Complexes 16a-f by Mass Spectroscopy and Elemental Analyses. The molecular formulae of the obtained complexes were proved according to the mass spectroscopic data and the elemental analyses. Physical data from the color, m.p., and yield in g (%) were illustrated, as shown in Table 1.

Elemental analyses and mass spectra indicated that the formed Cu(II)-complexes 16a-f resulted in the sum of the molecular weight of compounds 15a-f with one copper atom together with a Ph₃PO molecule.

Scheme 4. Mechanism Describes the Formation of Ligands 15a-f
The $^{13}$C NMR spectrum of 15a showed the carbonyl carbon signals at $\delta_C = 183.7$ and 183.6, whereas C=S resonated at $\delta_C = 176.7$ ppm. The ethyl carbons appeared at $\delta_C = 37.9$ for CH$_2$ and at $\delta_C = 175.4$ ppm. (C$_6$H$_4$CO) with a C=S carbon signal appeared at $\delta_C = 175.4$ ppm. The ethyl carbon signals resonated at $\delta_C = 176.7$ (CH$_3$)$_2$(CN) and 183.6 ppm (CH$_2$CN). Significantly, the exocyclic carbon signal (C=S) appeared in the $^{13}$C NMR spectrum of 15a at $\delta_C = 142.8$, whereas for 16a, it appeared at $\delta_C = 143.1$.

### 2.4. UV–Vis Studies

UV–vis absorption spectra of the Cu(II) complexes 16a–f were measured from 200 to 800 nm, using acetonitrile. The blue-colored compounds exhibited bands in UV–vis spectra, ranging from 540 to 584 nm (i.e., n→π*). These bands can be attributed to ligand-to-metal charge transfer transitions from nitrogen to Cu(II). N → Cu ← O bands are common in electronic spectra of metal complexes of thiosemicarbazides. Representative examples are the UV/vis spectra of compounds 16b and 16c (Figure 4). In the field of inorganic chemistry, UV/Vis spectra are usually associated with d–d transitions and colored transition metal complexes.

#### 2.5. Optimized Geometries

To verify the experimental findings, the complexes under study were optimized and are illustrated in Figure 5. No imaginary frequencies were noticed for the optimized complexes, ensuring that the obtained geometries were true minima. The energy differences ($\Delta E$) between the investigated complex ($E_i$) and the most stable one ($E_f$) are also given in Figure 5. The single point energies ensured the further favorability of complex 1 over other studied conformations.

#### 2.6. HS Analysis

HS analysis was considered a dependable technique to qualitatively elucidate intermolecular interactions within crystal structures and unveil the interactions around the molecules’ surface.31–34 HSs, including the $d_{norm}$ and its associated 2D fingerprints, shape index, and curvedness, were mapped for the studied complexes. Figure 6 shows the $d_{norm}$ map and the associated 2D fingerprint plots. The extracted shape index and curvedness maps are illustrated in Figure 7.

As shown in Figure 6(i), the C···H/ H···C contacts were noticed with obvious large red regions labeled 1 and exhibited 27.0% of the total HS area. Such contacts were also observed in the 2D fingerprint plots as a pair of symmetrical spikes at $(d_c + d_e) \sim 2.6$ Å (Figure 6(ii)).

The existence of red regions dubbed 2 in the HSs mapped over the $d_{norm}$ property could be attributed to the occurrence of the reciprocal O···H/ H···O contacts that were found in the 2D fingerprint plots at $(d_c + d_e) \sim 2.3$ Å. For S···H/ H···S contacts (labeled 3), prominent red regions were noticed with 2.1% of the total HS area and characterized by spikes at $(d_c + d_e) \sim 2.7$ Å. The N···H/ H···N contacts were observed with label 4, as white and red regions in the $d_{norm}$ maps, with a 2.1% contribution.

### Table 2. Stoichiometric Formation and Analytical Data of Cu-Complexes 16a–f

| ligand | metal salt | complex | stoichiometry | molecular formula | C, H, Cu, N, O, P, S |
|-------|------------|---------|--------------|-------------------|----------------------|
| 15a   | CuCl$_2$·2H$_2$O | 16a     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 67.15; H, 4.60; Cu, 7.25; N, 4.79; O, 5.48; P, 7.07; S, 3.66 found: C, 67.17; H, 4.62; Cu, 7.23; N, 4.77; O, 5.50; P, 7.05; S, 3.64 |
| 15b   | CuCl$_2$·2H$_2$O | 16b     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 67.60; H, 4.54; Cu, 7.15; N, 4.73; O, 5.40; P, 6.97; S, 3.61 found: C, 67.58; H, 4.56; Cu, 7.17; N, 4.71; O, 5.38; P, 6.95; S, 3.63 |
| 15c   | CuCl$_2$·2H$_2$O | 16c     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 69.11; H, 4.51; Cu, 6.77; N, 4.48; O, 5.11; P, 6.60; S, 3.42 found: C, 67.11; H, 4.53; Cu, 6.79; N, 4.50; O, 5.13; P, 6.58; S, 3.44 |
| 15d   | CuCl$_2$·2H$_2$O | 16d     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 67.44; H, 4.75; Cu, 7.14; N, 4.72; O, 5.39; P, 6.96; S, 3.60 found: C, 67.42; H, 4.77; Cu, 7.16; N, 4.70; O, 5.41; P, 6.98; S, 3.62 |
| 15e   | CuCl$_2$·2H$_2$O | 16e     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 67.60; H, 4.54; Cu, 7.15; N, 4.50; P, 6.97; S, 3.61 found: C, 67.62; H, 4.52; Cu, 7.13; N, 4.75; O, 5.42; P, 6.99; S, 3.59 |
| 15f   | CuCl$_2$·2H$_2$O | 16f     | 1:1          | C$_{14}$H$_{16}$CuN$_4$O$_2$P$_2$S | calcld: C, 67.72; H, 4.90; Cu, 7.03; N, 4.65; O, 5.31; P, 6.85; S, 3.54 found: C, 67.74; H, 4.92; Cu, 7.05; N, 4.63; O, 5.29; P, 6.85; S, 3.52 |
Concisely, the HS maps overlapped the shape index and curvuredness properties (Figure 7) confirmed the occurrence of the C−H/H−C, O−−H/−−O, S−−H/H−−N interactions by the existence of the complementary pair of red and blue triangles in the shape index and the flat green area in curvuredness.

3. EXPERIMENTAL SECTION

Uncorrelated Melting points were taken in a Gallenkamp melting point apparatus (Weiss-Gallenkamp, Loughborough, UK). The infrared spectra were recorded with the Bruker, IFS 88 instrument. Solids were measured by the attenuated total reflection (ATR) method. The positions of the respective transmittance bands are given in wave numbers $\nu$ [cm$^{-1}$] and were measured in the range from 3600 to 500 cm$^{-1}$. All UV−Vis spectra were recorded on the Spectord 50 Plus made by the company Q Analytik Jena (Thuringia, Germany). The NMR spectra of the title compounds described herein were recorded on a Bruker Avance 400 NMR instrument at 400 MHz for $^1$H NMR and 101 MHz for $^{13}$C NMR, and the references used were the $^1$H and $^{13}$C peaks of the solvent, acetone-$d_6$: 2.05 ppm for $^1$H NMR, and 206.26 ppm for $^{13}$C($^1$H)NMR spectra. For the characterization of centrosymmetric signals, the signal's median point was chosen; for multiplets, the signal range was given. The following abbreviations were used to describe the proton splitting pattern: d = doublet, t = triplet, m = multiplet, and dd = doublet of a doublet. The following abbreviations were used to distinguish between signals: $^\mathrm{H}$P = aromatic-CH. Signals of the $^{13}$C NMR spectra were assigned with the help of DEPT90 and DEPT135 and were specified in the following way: + = primary or tertiary carbon atoms (positive DEPT signal), − = secondary carbon atoms (negative DEPT signal), $^\mathrm{q}$q = quaternary carbon atoms (no DEPT signal). Mass spectra were observed by FAB (Fast atom bombardment) experiments and were recorded using the Finnigan, MAT 90 (70 eV) instrument. Elemental analyses were performed on the Elementar Vario MICRO instrument. TLC silica plates coated with a fluorescence indicator from Merck (silica gel 60 F254, thickness 0.2 mm) were used to purify the crude products, and flash chromatography with Silica gel 60 (0.040 x 0.063 mm, Gleduran) (Merck) was used. Solvents, including acetone-$d_6$, were purchased from Merck without further drying.

3.1. General Procedures. Compounds 14a-f were prepared according to the literature.$^{23}$

3.1.1. General Procedure for the Synthesis of Ligands 15a-f. 2,3-Dichloro-1,4-naphthoquinone (7) (250 mg, 1.10 mmol, 1.10 equiv) was added to a stirred solution of substituted hydrazinecarboxothioamides (14a-f) (1.00 mmol, 1.00 equiv) in 10 mL of dry CH$_2$CN. The resulting solution was stirred at room temperature for 16 h. After S-alkylation was complete (i.e. the reaction was followed up by TLC), the dried salt was redissolved in dry CH$_2$CN, after which Et$_3$N (1.10 mmol) and Ph$_2$P (1.10 mmol) were added. The resulting mixture was left under reflux for about 13−16 h. The reaction mixture was left to cool at room temperature, distilled H$_2$O (50 mL) was added, and the resulting solution was extracted with CH$_2$Cl$_2$. The organic extracts were dried over anhydrous CaCl$_2$, filtered, and evaporated. The crude material was purified by flash-chromatography using cyclohexane/ethyl acetate (4:1) to give compounds 15a-f.

3.1.1.1. (E)-2-(1,4-Dioxo-3-(triphenyl-κ-β-phosphanylidene)-3,4-dihydropyridazine-2(1H)-yldiene)-N-ethylhydrazine-1-carboxothioamide (15a). $R_f$ = 0.27 (cyclohexane/ethyl acetate; 4:1). Violet crystals (MeOH), 0.385 g (72%). mp: 210−212 °C. $^1$H NMR (400 MHz, Acetone-$d_6$): $\delta_H$ = 12.90 (s, 1H, NH$^-$), 7.93 (dt, $J$ = 44.4, 10.2 Hz, 2H, H$^\text{Ar}$), 7.84−7.88 (m, 2H, H$^\text{Ar}$), 7.65−7.71 (m, 15H, H$^\text{Ar}$), 5.77 (s, 1H, NH$^-$) 3.19−3.26 (m, 2H, CH$_2$ethyl$^\text{H}$), 0.62 ppm (t, $J$ = 7.1 Hz, 3H, CH$_2$ethyl$^\text{H}$). $^{13}$C($^1$H)NMR (101 MHz, Acetone-$d_6$): $\delta_C$ = 183.7 (C$_2$H$_2$CO), 183.6 (C$_2$H$_2$CO), 176.7 (C$_2$H$_2$CO), 142.8 (C$_2$H$_2$N), 137.2 (C$_2$H$_2$N), 137.1 (C$_2$H$_2$N), 134.5 (C$_2$H$_2$N), 134.1 (+, CH$^\text{Ar}$), 133.7 (+, CH$^\text{Ar}$), 133.6 (+, CH$^\text{Ar}$), 133.1 (+, CH$^\text{Ar}$), 132.8 (+, CH$^\text{Ar}$), 132.5 (+, CH$^\text{Ar}$), 132.4 (+, CH$^\text{Ar}$), 131.8 (+, 2CH$^\text{Ar}$), 131.7 (+, 2CH$^\text{Ar}$), 130.6 (+, CH$^\text{Ar}$), 129.1 (+, CH$^\text{Ar}$), 128.9 (+, CH$^\text{Ar}$), 128.6 (+, 2CH$^\text{Ar}$), 128.5 (+, 2CH$^\text{Ar}$), 126.6 (+, CH$^\text{Ar}$), 125.6 (C$_2$H$_2$N), 125.5 (C$_2$H$_2$N), 124.5 (C$_2$H$_2$N), 37.9 (−, CH$_2$ethyl$^\text{H}$), 13.5 ppm (+, CH$_2$ethyl$^\text{H}$). IR (ATR): $\tilde{\nu}$ = 3345, 3052 (w, NH), 1587, 1517 (m, C = O), 1435 (s, C = N), 1188 (s, C = P), 993 cm$^{-1}$ (s, C = S). MS (FAB, 3-NBA): $m/z$ (%) = 536 (100) [M + H]$^+$, 535 (30) [M + H]$^+$). $^{13}$C($^1$H)NMR (101 MHz, Acetone-$d_6$): $\delta_C$ = 184.7 (C$_2$H$_2$CO), 184.6 (C$_2$H$_2$N), 177.9 (C$_2$H$_2$N), 142.1 (C$_2$H$_2$N), 138.1 (C$_2$H$_2$N), 135.4 (C$_2$H$_2$N).
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Table 4. Chemical Shifts (δ) Including 1H and 13C NMR Spectroscopic Data for Ligand 1a and Its Complex 16a

| Signal    | 1H NMR (acetone-d6) | 13C NMR (acetone-d6) |
|-----------|----------------------|-----------------------|
| 16a       | 4.20 ppm (m, 2H, C\{H\}q) | 132.8 (+, C{\{H}\}Ar), 134.6 (+, CH\{\}\{\}), 133.7 (+, CH\{\}\{\}), 133.6 (+, 2x CH\{\}\{\}), 133.5 (+, 2x CH\{\}\{\}), 133.4 (+, CH\{\}\{\}), 132.4 (+, CH\{\}\{\}), 132.3 (+, CH\{\}\{\}), 130.6 (+, CH\{\}\{\}), 129.1 (+, 2x CH\{\}\{\}), 128.9 (+, 2x CH\{\}\{\}), 128.7 (+, CH\{\}\{\}), 128.6 (+, CH\{\}\{\}), 128.5 (+, CH\{\}\{\}), 128.3 (+, CH\{\}\{\}), 128.1 (+, CH\{\}\{\}), 127.7 (+, CH\{\}\{\}), 127.2 (+, CH\{\}\{\}), 126.6 (+, CH\{\}\{\}), 125.5 (+, CH\{\}\{\}), 125.2 (+, C{\{H}\}Ar), 46.3 ppm (−, C{\{H\}benzyl}). |
| IR (ATR): ν = 3347, 3055 (ν, NH), 1582, 1510 (s, C=O), 1433 (s, C= N), 1153 (s, C=P), 988 cm\(^{-1}\) (vs, C=C). MS (FAB, 3-NAH): m/z (%) = 598 (75) [M + H\(^{+}\)], 597 (30) [M\(^{+}\)]. HRMS (FAB, 3-NAH, C\(_{29}\)H\(_{36}\)N\(_{2}\)O\(_{2}\)P\(_{2}\)S\(_{3}\)) calcd: 598.1718; found: 598.1717. EA (C\(_{29}\)H\(_{36}\)N\(_{2}\)O\(_{2}\)P\(_{2}\)S\(_{3}\)) calcd: C, 72.35; H, 4.72; N, 7.03; O, 3.53; P, 5.18; S, 5.36. Found: C, 72.37; H, 4.74; N, 7.01; O, 3.53; P, 5.16; S, 5.34. |
| 15d       | 4.20 ppm (m, 2H, C\{H\}q) | 132.8 (+, C{\{H}\}Ar), 134.6 (+, CH\{\}\{\}), 133.7 (+, CH\{\}\{\}), 133.6 (+, 2x CH\{\}\{\}), 133.5 (+, 2x CH\{\}\{\}), 133.4 (+, CH\{\}\{\}), 132.4 (+, CH\{\}\{\}), 132.3 (+, CH\{\}\{\}), 130.6 (+, CH\{\}\{\}), 129.1 (+, 2x CH\{\}\{\}), 128.9 (+, 2x CH\{\}\{\}), 128.7 (+, CH\{\}\{\}), 128.6 (+, CH\{\}\{\}), 128.5 (+, CH\{\}\{\}), 128.3 (+, CH\{\}\{\}), 128.1 (+, CH\{\}\{\}), 127.7 (+, CH\{\}\{\}), 127.2 (+, CH\{\}\{\}), 126.6 (+, CH\{\}\{\}), 125.5 (+, CH\{\}\{\}), 125.2 (+, C{\{H}\}Ar), 46.3 ppm (−, C{\{H\}benzyl}). |
| IR (ATR): ν = 3347, 3052 (w, NH), 1580, 1507 (w, C=O), 1436 (s, C= N), 1188 (vs, C=P), 996 cm\(^{-1}\) (vs, C=S). MS (FAB, 3-NAH): m/z (%) = 550 (100) [M + H\(^{+}\)], 549 (28) [M\(^{+}\)]. HRMS (FAB, 3-NAH, C\(_{29}\)H\(_{36}\)N\(_{2}\)O\(_{2}\)P\(_{2}\)S\(_{3}\)) calcd: 550.1718; found: 550.1719. EA |
Figure 4. UV spectra of 16b and 16c in CH₃CN.

Figure 5. Optimized geometries of the studied complexes along with the energy difference (ΔE) between the investigated complex (E) and the most stable one (Eₘ).

(\text{C}_{13}\text{H}_{33}\text{Ni}_{2}\text{O}_{2}\text{PS}) \text{ calcd: C, 69.93; H, 5.14; N, 7.65; O, 5.82; P, 5.64; S, 5.83. Found: C, 69.95; H, 5.16; N, 7.63; O, 5.80; P, 5.62; S, 5.81.}

3.1.1.5. (E)-N-Cyclopropyl-2-(1,4-dioxo-3-(triphenyl-\(\approx\)-phosphanylidene)-3,4-dihydropthalalen-2(1H)-ylidene)-hydrazine-1-carbothioamide (15f). \(\text{R}_{2} = 0.28 \) (cyclohexane/ethyl acetate; 4:1). Violet crystals (MeOH), 0.426 g (78%). mp: 205–207 °C. \(\text{^1}H \text{ NMR} \) (400 MHz, acetone-d₆): \(\delta_H = \) 13.09 (s, 1H, NH\(^{\text{f}}\)), 8.41–8.14 (m, 4H, H\(^{27}\)), 8.11–7.80 (m, 3H, H\(^{28}\)), 7.80–7.43 (m, 12H, H\(^{29}\)), 5.99 (s, 1H, NH\(^{\text{f}}\)), 2.83–2.55 (m, 1H, CH\(_2\)C\(^{\text{cyclotropil}}\)), 0.71–0.51 ppm (m, 4H, 2× CH\(_2\)C\(^{\text{cyclotropil}}\)). \(\text{^1}C\{^1\text{H}\} \text{NMR} \) (101 MHz, acetone-d₆): \(\delta_C = 183.6 \) (C\(_\text{q}\) CO), 183.5 (C\(_\text{q}\) CO), 178.2 (C\(_\text{q}\) CS), 141.9 (C\(_\text{q}\) C=N), 137.2 (C\(_\text{q}\) C\(^{\text{q}}\)), 137.1 (C\(_\text{q}\) C\(^{\text{q}}\)), 134.6 (C\(_\text{q}\) C\(^{\text{q}}\)), 134.3 (+, CH\(^{\text{q}}\)), 134.2 (+, CH\(^{\text{q}}\)), 133.7 (+, CH\(^{\text{q}}\)), 133.6 (+, CH\(^{\text{q}}\)), 132.7 (+, CH\(^{\text{q}}\)), 132.5 (+, CH\(^{\text{q}}\)), 132.0 (+, CH\(^{\text{q}}\)), 131.9 (+, 2× CH\(^{\text{q}}\)), 131.8 (+, CH\(^{\text{q}}\)), 131.7 (+, CH\(^{\text{q}}\)), 130.6 (+, CH\(^{\text{q}}\)), 129.1 (+, CH\(^{\text{q}}\)), 129.0 (+, CH\(^{\text{q}}\)), 128.9 (+, CH\(^{\text{q}}\)), 128.8 (+, CH\(^{\text{q}}\)), 128.6 (+, CH\(^{\text{q}}\)), 128.5 (+, 2× CH\(^{\text{q}}\)), 126.5 (C\(_\text{q}\) C\(^{\text{q}}\)), 125.1 (C\(_\text{q}\) C\(^{\text{q}}\)), 124.2 (C\(_\text{q}\) C\(^{\text{q}}\)), 25.8 (+, CH\(_2\)C\(^{\text{cyclotropil}}\)), 6.5 ppm (~, 2× CH\(_2\)C\(^{\text{cyclotropil}}\)). \(\text{IR (ATR)}: \nu = 3342, 3050 \) (w, NH), 1580, 1511 (m, C=O), 1432 (s, C=N), 1186 (s, C=P), 996 cm\(^{-1}\) (s, C=S). MS (FAB, 3-NBA): m/z (%): 548 (100) [M + H\(^{+}\)], 547 (35) [M\(^{+}\)]. \(\text{HRMS} \) (FAB, 3-NBA, C\(_{32}\)H\(_{33}\)N\(_{2}\)O\(_{2}\)PS) calcd: 548.1562; found: 548.1563. EA (C\(_{32}\)H\(_{33}\)N\(_{2}\)O\(_{2}\)PS) calcd: C, 70.17; H, 4.79; N, 7.67; O, 5.84; P, 5.66; S, 5.85. Found: C, 70.17; H, 4.81; N, 7.69; O, 5.82; P, 5.64; S, 5.83.

3.1.1.6. (E)-N-Butyl-2-(1,4-dioxo-3-(triphenyl-\(\approx\)-phosphanylidene)-3,4-dihydropthalalen-2(1H)-ylidene)-hydrazine-1-carbothioamide (15f). \(\text{R}_{2} = 0.28 \) (cyclohexane/ethyl acetate; 4:1). Violet crystals (MeOH), 0.450 g (80%). mp: 195–197 °C. \(\text{^1}H \text{ NMR} \) (400 MHz, acetone-d₆): \(\delta_H = 13.18 \) (s, 1H, NH\(^{\text{f}}\)), 8.10–8.00 (m, 2H, H\(^{27}\)), 7.66–7.55 (m, 8H, H\(^{28}\)), 7.28–7.24 (m, 9H, H\(^{29}\)), 6.74 (s, 1H, NH\(^{\text{f}}\)), 3.58 (dd, J = 7.7, 1.5 Hz, 2H, CH\(_2\)butyl\(^{\text{f}}\)), 1.60–1.49 (m, 2H, CH\(_2\)butyl\(^{\text{f}}\)), 1.35–1.26 (m, 2H, CH\(_2\)butyl\(^{\text{f}}\)), 1.02–0.99 ppm (m, 3H, CH\(_3\)butyl\(^{\text{f}}\)). \(\text{^1}C\{^1\text{H}\} \text{NMR} \) (101 MHz, acetone-d₆): \(\delta_C = 186.1 \) (C\(_\text{q}\) CO), 185.9 (C\(_\text{q}\) CO), 178.4 (C\(_\text{q}\) CS), 142.3 (C\(_\text{q}\) C=N), 135.1 (C\(_\text{q}\) C\(^{\text{q}}\)), 134.6 (C\(_\text{q}\) C\(^{\text{q}}\)), 134.1 (C\(_\text{q}\) C\(^{\text{q}}\)), 132.7 (+, CH\(^{\text{q}}\)), 132.6 (+, CH\(^{\text{q}}\)), 131.3 (+, CH\(^{\text{q}}\)), 131.1 (+, CH\(^{\text{q}}\)), 130.7 (+, 3× CH\(^{\text{q}}\)), 130.5 (+, CH\(^{\text{q}}\)), 130.4 (+, CH\(^{\text{q}}\)), 129.9 (+, CH\(^{\text{q}}\)), 129.5 (+, CH\(^{\text{q}}\)), 129.4 (+, CH\(^{\text{q}}\)), 129.3 (+, CH\(^{\text{q}}\)), 128.7 (+, 2× CH\(^{\text{q}}\)), 128.1 (C\(_\text{q}\) C\(^{\text{q}}\)), 127.8 (C\(_\text{q}\) C\(^{\text{q}}\)), 127.7 (C\(_\text{q}\) C\(^{\text{q}}\)), 44.6 (~, CH\(_3\)butyl\(^{\text{f}}\)), 30.4 (~, CH\(_3\)butyl\(^{\text{f}}\)), 20.1 (~, CH\(_2\)butyl\(^{\text{f}}\)), 14.0 ppm (~, CH\(_2\)butyl\(^{\text{f}}\)). \(\text{IR (ATR)}: \nu = 3340, 3053 \) (w, NH), 1586, 1521 (m, C=O), 1434 (vs, C=N), 1170 (s, C=P), 992 cm\(^{-1}\) (s, C=S). MS (FAB, 3-NBA): m/z (%): 564 (100) [M + H\(^{+}\)], 563 (30) [M\(^{+}\)]. \(\text{HRMS} \) (FAB, 3-NBA, C\(_{32}\)H\(_{33}\)N\(_{2}\)O\(_{2}\)PS) calcd: 564.1875; found: 564.1873. EA (C\(_{32}\)H\(_{33}\)N\(_{2}\)O\(_{2}\)PS) calcd:
3.1.2. General Procedure for the Synthesis of Complexes 16a-f. A mixture of 15a-f (1.00 mmol, 1.00 equiv) with CuCl$_2$-
2H2O (0.170 g, 1.00 mmol, 1.00 equiv) and Ph2P (0.262 g, 1.00 mmol, 1.00 equiv) in 40 mL of absolute EtOH was stirred at room temperature for about 2–4 h (the reaction was monitored by thin-layer chromatography). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography using EtOAc/hexane (5:1) to afford compounds 16a–f.

3.1.2.1. (E)-(2-(1,4-Dioxo-3-(triphenyl-1,2,3-triazol-5-ylidene)-2-(1H)-ylidene)-1-ethylcarbazolamiothiyl)hydrazineyl ((triphenyl-1,2,3-triazol-5-ylidene)oxy) copper (16a). Rf = 0.35 (cyclohexane/ethyl acetate; 4:1). Deep blue crystals (MeOH), 0.718 g (82%). mp: 250–252 °C (decomp). 1H NMR (400 MHz, aceton-d6): δH = 7.73–7.65 (m, 15H, HAr), 7.64–7.58 (m, 6H, HAr), 7.56–7.50 (m, 13H, H), 5.49 (s, 1H, NH), 4.05 (q, J = 7.1 Hz, 2H, CH2ethyl), 1.20 ppm (t, J = 7.1 Hz, 3H, CH3ethyl). 13C[H]NMR (101 MHz, aceton-d6): δC = 170.0 (C0), 169.6 (C1), 165.4 (C2), 143.1 (C3, C4), 137.2 (C5, C6), 134.1 (+, 2x CH2), 133.6 (C7, C8), 133.5 (C9), 133.3 (+, 2x CH2), 131.9 (+, 6x CH1), 131.8 (+, 6x CH1), 131.7 (+, 6x CH1), 131.6 (+, 6x CH1), 129.1 (+, 3x CH), 129.0 (+, 3x CH), 128.6 (C16, C17), 128.5 (C16, C17), 39.0 (−, CH2ethyl), 13.6 ppm (−, CH2ethyl). IR (ATR): δ = 3054 (w, NH), 1576, 1576 (m, 15H, C0), 1482 (s, C=C), 1178 (s, C=P), 1019 (m, P=O), 995 (s, C=S), 536 (s, C=C), 457 cm−1 (s, C=O). MS (FAB, 3-NBA): m/z (%) = 897 (65) [M]+. HRMS (FAB, 3-NBA, C36H35CuN3O3P2S2MP [M]+) calcld: 897.1562; found: 897.1563. EA (C36H35CuN3O3P2S2) calcld: C, 67.60; H, 4.34; Cu, 7.15; N, 4.73; O, 5.40; P, 6.97; S, 3.61. Found: C, 67.58; H, 4.56; Cu, 7.17; N, 4.71; O, 5.38; P, 6.95; S, 3.63.

3.1.2.3. (E)-(1-Benzylcarbamothioyl)-2-(1,4-dioxo-3-(triphenyl-1,2,3-triazol-5-ylidene)-3,4-dihyronaphthalen-2(1H)-ylidene)hydrxazinyl ((triphenyl-1,2,3-triazol-5-ylidene)oxy) copper (16e). Rf = 0.36 (cyclohexane/ethyl acetate; 4:1). Deep blue crystals (MeOH), 0.872 g (93%). mp: 262–264 °C (decomp). 1H NMR (400 MHz, aceton-d6): δH = 8.25–7.75 (m, 4H, HAr), 7.74–7.62 (m, 15H, HAr), 7.61–7.59 (m, 15H, HAr), 7.38–7.07 (m, 3H, HAr), 3.63–4.43 ppm (2H, 2x CH2benzyl). 13C[H]NMR (101 MHz, aceton-d6): δC = 172.6 (C0, CO), 172.4 (C0, CO), 170.9 (C3, CS), 143.5 (C5=C=S), 137.1 (C4, C5), 134.9 (C1), 134.4 (C6), 133.9 (C7, C8), 133.0 (+, CH2), 130.2 (+, CH2), 130.7 (+, CH2), 130.4 (+, CH2), 129.8 (+, CH2), 129.2 (+, 4x CH2), 129.4 (+, 4x CH2), 128.9 (+, CH2), 128.3 (+, 2x CH2), 128.2 (+, 2x CH2), 127.7 (+, 2x CH2), 127.1 (+, 2x CH2), 126.8 (+, CH2), 126.4 (+, CH2), 126.1 (+, CH2), 125.9 (+, CH2), 125.8 (+, CH2), 125.3 (C3, C4), 125.2 (C5, C6). 13C[H]NMR (101 MHz, aceton-d6): δC = 67.1, 61.9; H, 4.51; Cu, 6.77; N, 4.48; O, 5.11; P, 6.60; S, 3.42. Found: C, 67.11; H, 4.53; Cu, 6.79; N, 4.50; O, 5.13; P, 6.58; S, 3.44.

3.1.2.4. (E)-(2-(1,4-Dioxo-3-(triphenyl-1,2,3-triazol-5-ylidene)-1,3-dihyronaphthalen-2(1H)-ylidene)ethylcarbazolamiothiyl)hydrazineyl ((triphenyl-1,2,3-triazol-5-ylidene)oxy) copper (16d). Rf = 0.31 (cyclohexane/ethyl acetate; 4:1). Deep blue crystals (MeOH), 0.712 g (80%). mp: 268–270 °C. 1H NMR (400 MHz, aceton-d6): δH = 7.98–7.68 (m, 13H, HAr), 7.63–7.57 (m, 6H, HAr), 7.56–7.47 (m, 15H, HAr), 5.63 (s, 1H, NH), 4.23–3.85 (s, 1H, CHprop), 1.45–1.23 ppm (6H, 2x CHprop). 13C[H]NMR (101 MHz, aceton-d6): δC = 173.1 (C0, CO), 172.9 (C0, CO), 170.1 (C3, CS), 144.4 (C5=C=S), 135.2 (C4), 134.1 (C6), 133.7 (C7, C8), 133.4 (+, CH2), 132.8 (+, 5x CH2), 132.7 (+, 5x CH2), 132.6 (+, 5x CH2), 132.5 (+, 5x CH2), 132.4 (+, CH2), 132.5 (+, CH2), 129.8 (+, CH2), 129.5 (+, 5x CH2), 129.3 (+, 5x CH2), 127.0 (C3, C4), 126.7 (C9, C10), 46.4 (+, CHprop), 22.7 ppm (−, 2x CHprop). IR (ATR): δ = 3054 (w, NH), 2997, 1515, 1513 (m, 15H, C0), 1483 (s, C=C), 1163, 1153 (m, C=C), 1026 (w, CO), 996 (m, C=S), 537 (vs, Cu–N), 449 cm−1 (s, Cu–O). MS (FAB, 3-NBA): m/z (%) = 899 (55) [M]+. HRMS (FAB, 3-NBA, C36H35CuN3O3P2S2MP [M]+) calcld: 899.1713; found: 899.1716. − EA (C36H35CuN3O3P2S2) calcld: C, 67.44; H, 4.75; Cu, 7.14; N, 4.72; O, 5.39; P, 6.96; S, 3.60. Found: C, 67.42; H, 4.77; Cu, 7.16; N, 4.70; O, 5.41; P, 6.98; S, 3.62.

3.1.2.5. (E)-(1-Cyclopropylcarbamothioyl)-2-(1,4-dioxo-3-(triphenyl-1,2,3-triazol-5-ylidene)-3,4-dihyronaphthalen-2(1H)-ylidene)hydrxazinyl ((triphenyl-1,2,3-triazol-5-ylidene)oxy) copper (16e). Rf = 0.32 (cyclohexane/ethyl acetate; 4:1). Deep blue crystals (MeOH), 0.763 g (86%). mp: 249–251 °C.
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SHELXL-2014 (full-matrix least-squares on N), 1159 (vs, C at 123(2) K or 298(2) K using Cu-Kα radiation (Å). Dual space methods (SHELXT).

Cu, 7.05; N, 4.63; O, 5.29; P, 6.85; S, 3.52.

Carboxylic acids, 
C$_{13}$H$_{20}$N$_2$O$_4$PS, M$_r$ = 1113.23, crystal size: 0.18 × 0.12 × 0.03 mm, triclinic, space group P1 (no. 2), α = 18.6988(5) Å, b = 18.8744(5) Å, c = 20.8063(6) Å, α = 103.938(2)°, β = 103.303(2)°, γ = 116.775(2)°, V = 5856.8(3) Å$^3$, Z = 4, ρ = 1.26 Mg/m$^3$, μ(Cu-Kα) = 176 mm$^{-1}$, F(000) = 2336, T = 298 K, 2θ$_{max}$ = 144.6°, 96,411 collected data, merged to 23,046 unique reflections (using a HKLFS file), 1411 parameters, 2775 restraints (see cif-file for details), R$_{I}$ = 0.065 (for 18,260 I > 2σ(I), wR$_{I}$ = 0.211 (all data), S = 1.03, largest diff. peak/hole = 0.95/−0.47 e Å$^{-3}$.

CCDC 2182411 (15c) and 2182412 (15f) contain 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.

4. COMPUTATIONAL METHODS

4.1. Geometrical Optimization and Energy Calculations. Various quantum mechanical calculations were carried out to confirm the experimental results. The studied complexes were first optimized at the B3LYP/6-31G* level of theory.

The vibrational frequency and single-point energy calculations were performed upon the optimized geometries. All the adopted quantum mechanical calculations were executed at the B3LYP/6-31G* level of theory with the help of Gaussian 09 software.

4.2. HS Analysis. In the current study, HS analysis was executed to give an in-depth qualitative insight into the role of the main intermolecular interactions. Using HS analysis, the normalized contact distance ($d_{norm}$) surface was mapped over a fixed color scale ranging from red (−0.05 au) to blue (0.75 au). The fingerprint plots were generated using the translated 1.0–2.8 Å range, and reciprocal contacts were considered. Moreover, the shape index and curvedness properties were mapped with the range of color from 1.0 au (concave) to 1.0 au (convex) and a range of −4.0 au (flat) to 0.40 au (singular), respectively. The generated HSs and the associated 2D fingerprint plots were extracted using the CrystalExplorer17 software.

5. CONCLUSION

New (E)-(1-(4,4-dioxo-2-(tri-phenylphosphanylidene)-3,4-dihydronaphthalen-2-ylidene)-hydrozine-1-carbothioamide were obtained during a one-pot reaction of 2,3-dichloro-1,4-naphthoquinone with thiosemicarbazides, triphénylphosphine (Ph$_3$P) in the presence of triethylamine (Et$_3$N) as a catalyst. The reaction was a type of Eschenmoser nucleophilic addition. Utilizing the newly prepared ligands, their complexation with CuCl$_2$ and Ph$_3$P was investigated. Autoxidation occurs, and (E)-(2-(1,4-dioxo-3-(triphenyl-phosphanylidene)-3,4-dihydronaphthalen-2-ylidene)-carbamothioyl)hydrizinyl)({(triphenylphosphanyloxy)couper
derivatives were formed in very good yields. Quantum mechanical calculations using the DFT method confirmed the stability of the obtained complexes.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04113.

NMR (1H NMR and 13C NMR), IR, and mass spectra, in addition to HRMS spectra of compounds 15a-f and 16a-f; figures of UV Spectra of compounds 16a-f; and X-ray figures and structural data of and compounds 15c and 15f (PDF)

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Notes
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