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Tungsten pentacarbonyl complexes of 1,3-benzoxaphospholes

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ABSTRACT

2-R-1,3-Benzoxaphospholes (R-BOPs) are examples of fluorescent conjugated materials possessing low coordinate phosphorus centers. A series of 2-(p-XC$_6$H$_4$)-BOPs (X = H, Cl, Br, Me, OMe) react with [W(CO)$_5$(NCMe)] to produce the crystalline complexes [W(CO)$_5$(2-Ar-BOP)] (**2a**-**e**). All complexes were characterized by NMR spectroscopy and by single crystal X-ray diffraction. The crystal structures all displayed extensive π-stacking of the BOP ligands and gear locking of the CO groups. Addition of the protecting [W(CO)$_5$] group to the BOPs was discovered to significantly diminish fluorescence of the BOP moiety.

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1. Introduction

Over the past decade, considerable effort has focused on the synthesis of new organic π-conjugated systems for optoelectronic applications such as organic photovoltaic cells (OPVs), organic light-emitting diodes (OLEDs) and organic field effect transistors (OFETs) [1]. Explorations of related materials featuring main group elements are well under way. In particular, materials which based on heterocyclopentadiene rings, such as thiophenes, pyrroles, and phospholes are fairly well developed. Organophosphorus compounds, in particular σ^3,λ^3-phospholes, have proved very interesting since they possess a phosphorus lone pair of electrons, thus allowing further reactivity [2]. Chemical modification of the P atom by oxidation, alkylation, or coordination by Lewis acids and metals has led to tunable new π-conjugated systems with diverse photo physical properties [3].

π-Conjugated compounds featuring pπ-pπ bonded phosphorus are one emerging subclass of materials with the potential for possessing interesting optoelectronic properties [4]. Most of these materials, however, do not display significant luminescent properties. Some recent notable exceptions (Chart 1) include 2-R-1,3-benzoxaphospholes (R-BOPs) [5], benzobisoxaphospholes (A) [5], naphthoxaphospholes (B) [6], napthabisoxaphospholes (C) [7], benzothiaphospholes (D) [8], benzobisthiaphospholes (E) [9] and triazaphospholes (F-G) [10]. These aromatic heterocycles feature five-membered aromatic ring systems containing P=C bonds, allowing a greater participation of the phosphorus center in π conjugation [4,11]. Our group has also explored integration of multiple 2-aryl-1,3-benzoxaphosphole units across other aromatic spacers and the impact on fluorescence properties [12].

As part of our effort to further elaborate the chemistry of R-BOPs, we have begun studies to extend the π-conjugation using catalytic C-C coupling reactions. However, our initial attempts to conduct Suzuki-Miyaura reactions yielded several unidentified products instead of the desired coupling product. These results suggest that it may be necessary to protect the P=C bond. In the early 90s, Mathey et al. have successfully employed the tungsten pentacarbonyl group as a removable protecting group to coordinate (and stabilize) P=C bonds for a range of interesting molecules [13]. However, structural studies of phosphorus heterocycles forming P-coordinated complexes are somewhat limited. Some examples of [W(CO)$_5$] coordinated complexes include phosphinine derivatives (H) [14], phospholes (I) [3,15] and 1*H*-1,3-benzazaphospholes (J) [16] (Chart 2).

Herein, we have reported the synthesis and structural characterization of five (2-Ar-1,3-benzoxaphosphole)pentacarbonyltungsten(0) complexes. The impact of tungsten(0) coordination on the luminescence properties was also examined.

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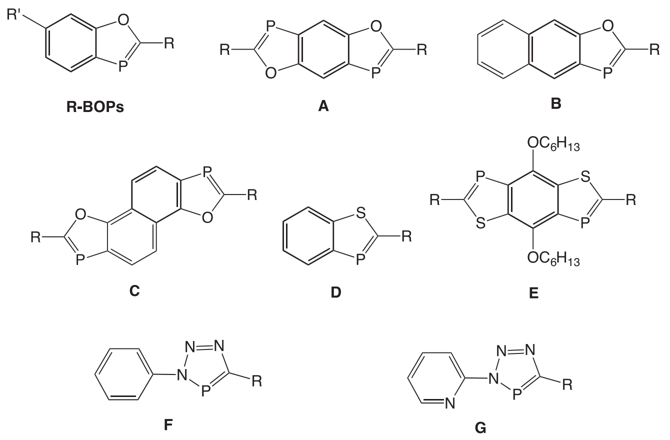

Chart 1. Examples of luminescent organophosphorus compounds featuring P=C bonds.

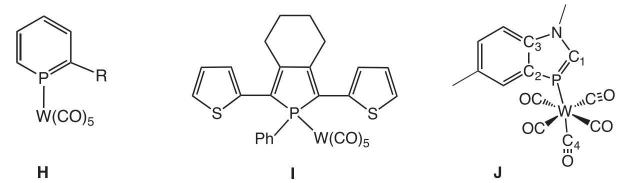

Chart 2. Structural examples of organophosphorus compounds coordinated to a pentacarbonyltungsten derivative.

2. Experimental

2.1. General materials and methods

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using a Schlenk line or in a MBraun Labmaster 130 glove box. Dry THF and toluene were obtained from a MBraun SPS-800 solvent drying and purification system using filter material MB-KOL-A. Acetonitrile was dried prior to use from calcium hydride. Tungsten hexacarbonyl was purchased from Sigma Aldrich and used as received. Acetonitrile pentacarbonyltungsten (0) [17] and all 2-R-1,3-benzoxaphospholes ligands (**1a-e**) [5] were prepared according to literature procedure.

2.2. Synthesis of η^1-[2-phenyl-1,3-benzoxaphosphole-P] pentacarbonyl-tungsten(0) complex (**2a**)

In a glove box, 2-phenyl-1,3-benzoxaphosphole (0.137 g, 0.644 mmol) and acetonitrile pentacarbonyltungsten (0) (0.235 g, 0.644 mmol) were added to a 20 mL vial. Dry THF (1 mL) was added and the vial was capped and sealed with electrical tape. The solution turned orange. The solution vial was brought out of the glove box and heated at 50 °C for 5 min, before being placed in a 4 °C fridge to crystallize. After 18 h, orange crystals had formed. The vial was brought into the glove box. The crystals were isolated by filtration and washed with THF before being dried in vacuum. Yield: 0.057 g (17%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 62.9 ($^1J_{PW} = 262.8$ Hz). ^1H NMR (CD_2Cl_2): δ 8.10 (dd, $J = 7.4$, 2.6 Hz, 2H), 7.95 (t, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.61 (t, $J = 7.8$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.46 (m, 2H). Anal. Calcd for $C_{18}H_9O_6PW$ (536.08): C, 40.33; H, 1.69. Found: C, 40.92; H, 1.62.

2.3. Synthesis of η^1-[2-(p-chlorophenyl)-1,3-benzoxaphosphole-P] pentacarbonyl-tungsten(0) complex (**2b**)

The compound **2b** was prepared as described for **2a**, with 2-(*p*-chlorophenyl)-1,3-benzoxaphosphole (0.140 g, 0.567 mmol) and acetonitrile pentacarbonyltungsten (0) (0.207 g, 0.567 mmol) as reactants. Yield: 0.137 g (42%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 65.8 ($^1J_{PW} = 266.6$ Hz). ^1H NMR ($CDCl_3$): δ 8.02 (dd, $J = 8.7$, 2.7 Hz, 2H), 7.91 (t, $J = 7.5$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.62–7.55 (m, 1H), 7.51–7.46 (m, 2H), 7.43 (td, $J = 7.5$, 3.0 Hz, 1H). Anal. Calcd for $C_{18}H_8O_6ClPW$ (570.52): C, 37.89; H, 1.41. Found: C, 37.46; H, 1.14.

2.4. Synthesis of η^1-[2-(p-bromophenyl)-1,3-benzoxaphosphole-P] pentacarbonyl tungsten (0) complex (**2c**)

The compound **2c** was prepared as described for **2a**, with 2-(*p*-bromophenyl)-1,3-benzoxaphosphole (0.439 g, 1.51 mmol) and acetonitrile pentacarbonyltungsten (0) (0.550 g, 1.51 mmol) as reactants. Yield: 0.390 g (42%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 66.4 ($^1J_{PW} = 264.9$ Hz). ^1H NMR (CD_2Cl_2): δ 8.01–7.91 (m, 3H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.62 (t, $J = 8.8$, 1.6 Hz, 1H), 7.45 (td, $J = 7.5$, 3.0 Hz, 1H). Anal. Calcd for $C_{18}H_8O_6BrPW$ (613.88): C, 35.16; H, 1.31. Found: C, 35.41; H, 1.46.

2.5. Synthesis of η^1-[2-(p-tolyl)-1,3-benzoxaphosphole-P] pentacarbonyl tungsten (0) complex (**2d**)

The compound **2d** was prepared as described for **2a**, with 2-(*p*-tolyl)-1,3-benzoxaphosphole (0.133 g, 0.589 mmol) and acetonitrile pentacarbonyltungsten (0) (0.215 g, 0.589 mmol) as reactants. Yield: 0.075 g (23%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 58.3 ($^1J_{PW} = 263.3$ Hz). ^1H NMR (CD_2Cl_2): δ 7.99 (dd, $J = 8.3$, 2.8 Hz, 2H), 7.93 (t, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.62–7.54 (m, 1H), 7.43 (td, $J = 7.5$, 3.1 Hz, 1H), 7.34 (d, $J = 7.9$ Hz, 2H), 2.42 (m, 3H). Anal. Calcd for $C_{19}H_{11}O_6PW$ (550.10): C, 41.48; H, 2.02. Found: C, 41.74; H, 1.95.

2.6. Synthesis of η^1-[2-(p-methoxyphenyl)-1,3-benzoxaphosphole-P]pentacarbonyl tungsten (0) complex (**2e**)

The compound **2e** was prepared as described for **2a**, with 2-(*p*-methoxyphenyl)-1,3-benzoxaphosphole (0.166 g, 0.685 mmol) and acetonitrile pentacarbonyltungsten (0) (0.250 g, 0.685 mmol) as reactants. Yield: 0.106 g (27%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.5 ($^1J_{PW} = 260.6$ Hz). ^1H NMR (CD_2Cl_2): δ 8.05 (dd, $J = 9.0$, 2.7 Hz, 2H), 7.92 (t, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.60–7.53 (m, 1H), 7.42 (td, $J = 7.5$, 3.0 Hz, 1H), 7.04 (d, $J = 8.6$ Hz, 2H), 3.88 (s, 3H). Anal. Calcd for $C_{19}H_{11}O_7PW$ (566.10): C, 40.31; H, 1.96. Found: C, 39.78; H, 1.81.

3. Results and discussion

3.1. Synthesis and characterization

A series of 2-Ar-1,3-benzoxaphosphole complexes **2a-e** are readily obtained as orange air-stable crystals in moderate yields (17%–42%, Table 1) by heating solutions of [W(CO_5)(NCMe)] [17] with 2-Ar-1,3-benzoxaphospholes (Ar-BOPs) **1a-e** in THF to 50 °C for 5 min and then cooling overnight to 4 °C (Scheme 1).

Table 1
Yields, $^{31}P\{^1H\}$ NMR chemical shifts, and $^1J_{PW}$ coupling constant for complexes **2a-e.**

	X	Yield (%)	^{31}P δ (ppm)	$^1J_{PW}$ (Hz)
2a	H	17	62.8	262.8
2b	Cl	42	65.8	266.6
2c	Br	42	66.4	264.9
2d	Me	23	58.2	263.3
2e	OMe	27	52.4	260.6

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